Appendix A

Analytical Methods
Ongoing Quality Control
Storage Stability

CALIFORNIA DEPT. OF FOOD & AGRICULTURE
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Method #: 7.0
Original Date: May 19, 1999
Revised Date: October 16, 2000

Determination of Bifenthrin in Water by GC/ECD

Scope: This method is for the determination of bifenthrin in water. The reporting limit of this method is 0.05 ppb.

Principle: The water is extracted with ethyl acetate. The extract is then dried with sodium sulfate. The dried extract is concentrated and analyzed by gas chromatography with an electron capture detector (ECD).

Reagents, Equipment and Instrument:

Reagents:

1. Bifenthrin, CAS# 82657-04-3, 1.0 mg/mL in acetone, obtained from CDFA Standard Repository (Center for Analytical Chemistry, California Department of Food and Agriculture)
2. Ethyl acetate, pesticide residue grade
3. Sodium sulfate, anhydrous, granular, ACS 10-60 mesh

Equipment:

1. Separatory funnels, 1000 mL
2. Beakers, 600 mL
3. Boiling flasks, flat-bottomed, 24/40 joints, 500 mL
4. Rotary evaporator, Büchi-Brinkmann, Model RE 111
5. Graduated conical test tubes, 15 mL
6. Nitrogen evaporator, Organomation, Model 112
7. Vortex mixer, Fisher Scientific, Model Vortex-Genie 2

Instrument:

1. GC: Hewlett Packard 5890 Series II gas chromatograph with ECD
2. Column: HP-1, 30 m x 0.53 mm x 2.65um

Analysis:

Sample Extraction:

1. Remove samples from refrigerated storage and allow them to come to room temperature (± 5 °C).
2. Shake each sample, weigh out 500 ± 1 grams or record sample weight. Place this aliquot into a 1-liter separatory funnel.
3. Extract samples by adding 120 mL of ethyl acetate and shaking vigorously for two minutes. **Vent frequently to relieve pressure.**
4. After the layers have separated, drain the aqueous layer into a 600-mL beaker.
5. Pour the organic layer from the top of the separatory funnel into a 500-mL boiling flask through a funnel filled with 20 g of anhydrous sodium sulfate.
6. Transfer the aqueous layer back to the separatory funnel.
7. Repeat steps 3 through 6 two more times with 100 mL of ethyl acetate. Combine the ethyl acetate extract.
8. Rinse the sodium sulfate twice with 20 mL of ethyl acetate and combine in the flask.
9. Concentrate the extract to ~ 2 mL on a rotary evaporator using 50 °C water bath and a vacuum of 23 inches Hg.
10. Transfer the concentrated extract into a calibrated conical test tube.
11. Rinse the flask twice with 2 mL of ethyl acetate each and combine the extract.
12. Place extract on a nitrogen evaporator with a 45 °C water bath and evaporate to 1.0 mL under a gentle stream of nitrogen.
13. Vortex for about 15 seconds and transfer the contents into an autosampler vial for analysis.

Instrument Conditions:

Primary analysis:

Instrument: Hewlett Packard 5890 Series II gas chromatograph with ECD, a 7673 autosampler and HP 3365 Series II ChemStation (Version A.03.21)
Column: HP-1, 30 m x 0.53 mm x 2.65 µm
Injector: 220 °C
Detector: 320 °C
Oven temperature program: Initial 120 °C, held 1 minute
Rate 20 °C/minute
Final 280 °C, held 15 minutes
Volume injected: 2 µL
Retention Time: approximately 15.7 ± 0.1 minutes

Confirmation analysis:

Instrument: Hewlett Packard 6890 Series gas chromatograph with mass selective detector (MSD) and HP ChemStation (Version B.02.06)
Column: HP-5MS, 30 m x 0.25 mm x 0.25 µm
Injector: 250 °C
Detector: 280 °C

Confirmation analysis: continued

Oven temperature program: Initial 70 °C, held 1 minute
Rate 20 °C/minute
Final 260 °C, held 10 minutes

SIM parameters: 165, 166, 181

Volume injected: 1 μL

Retention Time: approximately 13.9 ± 0.1 minutes

Calculations:

$$ppb = \frac{(\text{sample peak ht.})(\text{response factor, } \eta g)(\text{sample final vol., mL})(1000\mu L/mL)}{(\text{sample vol. injected, } \mu L)(\text{sample wt., g})}$$

$$\text{where: response factor } (\eta g) = \frac{\Sigma[(\text{std. conc.}_n, \eta g/\mu L)\ (\text{std. vol. injected, } \mu L)/\ (\text{std. peak ht.}_n)]}{n}$$

n = number of standards

Method Performance:

Quality Control:

1. A 4-point calibration curve of 0.02, 0.05, 0.1, and 0.2ηg/μL bifenthrin was obtained at the beginning and the end of each set of samples for calculating the response factor.
2. Each sample shall be injected two times to insure reliability of the analysis. If the signal of a sample is greater than that of the highest standard in the calibration curve, dilute the sample. Re-inject the diluted sample together with standards twice more. A sample set is usually comprised of 12 ~ 14 samples, a blank and a spike.

Method Detection Limit (MDL):

Method Detection Limit (MDL) refers to the lowest concentration of analyte that a method can detect reliably in either a sample or a blank. To determine the MDL, spike 7 samples, 500 ± 1 g of background water each, with 0.1 ppb of bifenthrin for the surface water and 0.2ppb of bifenthrin for the well water and process each through the entire method along with a blank. The standard deviation was computed from the 7 results (ppb). The MDL was computed as follows:

$$MDL = t_{(n-1,\ 1-\alpha\ =\ 0.99)}S$$

Where: $t_{(n-1,\ 1-\alpha\ =\ 0.99)}$ = the student "t" value for the 99% confidence level with n-1 degrees of freedom (for seven replicates, t = 3.143 with 6 degrees of freedom)

n = the number of replicates

S = the standard deviation obtained from replicate analysis

The results for the standard deviations and MDL are in Appendix, Table 1and 2.

Reporting Limit (RL):

Reporting Limit (RL) refers to level above which quantitative results may be obtained. In this method the RL is set at 0.05 ppb for bifenthrin.

Recovery Data:

In surface water, preparing five sets of method validation samples. Each set contained a blank and four levels of spikes. In well water, preparing three sets of method validation samples. Each set contained a blank and three levels of spikes. The background water (American River water or well water) was obtained from Department of Pesticide Regulation. Each set was extracted by a different person or on separate days. Recovery of bifenthrin is shown in Appendix, Table 3 and 4.

Discussion:

Starting from the beginning, both methylene chloride and ethyl acetate were successfully developed for extraction. Due to environmental concern, we decided to extract residue using ethyl acetate. When we analyzed the samples, a column of HP-5, 30 m x 0.53 mm x 2.65 um was used for analysis because the HP-1 column was not available. Bifenthrin was detected at 9.2 ± 0.1 minutes with an isotherm 280 °C temperature. The recovery of the spiking was 84.4% and the positive result was confirmed with MSD. Therefore, the HP-5 column could also be used in this method.

References:

Vincent Quan, *Bifenthrin,* Worker Health & Safety Laboratory, Center for Analytical Chemistry, California Department of Food and Agriculture.

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Appendix: Table 1. Bifenthrin Spike Results (ppb) for MDL Determination in surface water

0.1ppb Spike #	**Bifenthrin** (ppb)
1	0.0986
2	0.0929
3	0.0855
4	0.0895
5	0.0811
6	0.103
7	0.119
S =	0.0127 ppb
MDL = 3.143 x S =	0.0399 ppb

Table 2. Bifenthrin Spike Results (ppb) for MDL Determination in well water

0.1ppb Spike #	**Bifenthrin** (ppb)
1	0.206
2	0.201
3	0.209
4	0.194
5	0.192
6	0.190
7	0.215
S =	0.00945 ppb
MDL = 3.143 x S =	0.0297 ppb

Table 3. Bifenthrin Method Validation Results and Recovery in surface water

	Bifenthrin	
Spike Level (ppb)	Result (ppb)	Recovery (%)
0.1	0.0965	96.5
	0.104	104
	0.0876	87.6
	0.125	125
	0.0940	94.0
5.0	4.83	96.6
	5.30	106
	4.54	90.8
	5.15	103
	5.11	102
20	18.0	90.0
	19.4	97.0
	15.8	79.0
	14.8	74.0
	18.4	92.0
50	45.4	90.8
	50.3	101
	47.1	94.2
	47.1	94.2
	49.0	98.0

Table 4. Bifenthrin Method Validation Results and Recovery in well water

	Bifenthrin	
Spike Level (ppb)	Result (ppb)	Recovery (%)
0.1	0.0857	85.7
	0.0932	93.2
	0.0797	79.7
1.0	0.792	79.2
	0.821	82.1
	0.758	75.8
10	8.79	87.9
	8.61	86.1
	8.15	81.5

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Method #: EM32.1
Original Date: April 30, 1999
Revised Date: July 10, 2000

Fenoxycarb, Pyriproxyfen and Hydramethylnon in Water

Scope: This method is for the determination of Fenoxycarb, Pyriproxyfen and Hydramethylnon in surface and well water. The reporting limit of this method for Fenoxycarb and Pyriproxyfen is 0.1ppb, and for Hydramethylnon is 0.2ppb.

Principle: Fenoxycarb, Pyriproxyfen and Hydrameyhylnon in water are extracted with methylene chloride. After the solvent evaporated, the extract is dissolved in methanol. All three compounds are determined by HPLC using an UV detector.

Reagents:

1. Fenoxycarb, CAS#79127-80-3, 1.0 mg/mL in methanol, obtained from CDFA Standard Repository (Center for analytical Chemistry, California Department of Food and Agriculture).
2. Pyriproxyfen, CAS# 95737-68-1, 1.0 mg/mL in methanol, obtained from CDFA Standard Repository (Center for analytical Chemistry, California Department of Food and Agriculture)
3. Hydramethylnon, CAS#67485-29-4,1.0 mg/mL in methanol, obtained from CDFA Standard Repository (Center for analytical Chemistry, California Department of Food and Agriculture)
4. Methylene chloride, pesticide residue grade,
5. Methanol, pesticide residue grade
6. Water, HPLC grade
7. Acetonitrile, HPLC grade
8. Buffers:

A: In 1000mL	B: In 500mL
90mL HPLC water	471mL HPLC water
900mL Methanol	25mL Methanol
10mL 1M Ammonium formate	4.75mL 1M Ammonium formate
1mL Formic Acid	0.5mL Formic acid

Safety:

1. Most of the reagents used and analyzed for in this method have not been completely characterized. All general laboratory safety rules must be followed.
2. Methylene chloride may consider be a carcinogen, please handle it with extremely caution.

Equipment:

1. Separatory funnels, 1000 mL
2. Boiling flasks, flat-bottomed, 24/40 joints, 500 mL
3. Funnels, glass short stemmed 100 mm diameter

Equipment: (continuous)

4. Rotary evaporator, Büchi-Brinkmann, Model R 110
5. Conical test tubes, graduated, calibrated 15 mL
6. Nitrogen evaporator, Organomation, Model 12
7. Vortex mixer, Thermolyne, Model 37600
8. Acrodisc®, Gelman, 25 mm x 0.2 µm, disposable filter
9. Syringe, Hypodermic, 5 or 10 mL

Instruments:

1. HPLC: Hewlett-Packard 1050 Liquid Chromatographs with a ChemStation and UV detector.
2. Analytical columns: Beckman Ultrasphere 5 µm, 4.6mm, 25 cm in length and Pickering column for carbamate analysis 5µm, 4.6mm, 25cm in length.

Interference:

1. The UV detector has limited specificity. The coleution interference may occur.
2. All positive samples will be confirmed on LC/MS.

Standard Preparation:

1. After received the standard mix containing 1mg/mL of each compound from CDFA Standard Repository, the standard mix is diluted to 10ηg/µl with methanol as a working standard.
2. Dilute the working standard into a series of desired standard set that will be used for instrument calibration and samples calculation.
3. Keep all prepared standards in the designated refrigerator for storage while not in use.
4. The shelf life of each prepared standard is six months.

Sample Preservation and Storage:

1. Check the temperature of samples upon arrived and records it in the notebook for temperature.
2. Sign the chain custody and obtain the EMON number from supervisor.
3. Store all samples in the walk-in refrigerator waiting for analysis.

Test Sample Preparation:

1. Remove samples from storage and allow them to come to room temperature (± 5 °C).
2. Shake each sample well and weigh out approximately 500 grams by difference. Place this aliquot into a separatory funnel. Unused sample will be restored in the walk-in refrigerator.
3. Extract samples by adding 100 mL of methylene chloride and shake vigorously for one minute. **Vent frequently to relieve pressure.**
4. After phase separation, drain the methylene chloride through a glass funnel containing 15 grams of Na_2SO_4 and glass wool under. Collect the extract into a boiling flask.
5. Repeat steps 3 and 4 two more times with 80 mL of methylene chloride each.
6. After the final extract drained, rinse the sodium sulfate with 25 mL of methylene chloride.
7. Concentrate the extract to 2 ~ 3 mL on a rotary evaporator using 30 ~ 35 °C water bath and a vacuum of 15 inches Hg.
8. Filter the extract through an Acrodisc® unit and collect the filtrate in a calibrated 1mL conical test tube.
9. Rinse the flask two times with 3 mL of methanol each. Filter through the same Acrodisc® unit and collect the rinse in the same test tube.

Test Sample Preparation: (continuous)

10. Place the extract in a nitrogen evaporator with water bath set at 45 °C and evaporate just to a mark for 1mL. (If below 1mL mark, add methanol to bring up to 1mL)
11. Votex the tube for 15 second and transfer the content into two autosampler vials with inserts for analysis.

Instrument Conditions:

For Fenoxycarb and Pyriproxyfen,

Instrument:	HPLC, Hewlett- Packard Model 1050, controlled by Chemstation
Column:	Beckman Ultrasphere 5 μ, 4.6 mm, 25 cm long
Mobile phase:	Isocratic 20% water and 80% acetonitrile
Flow:	1.0 mL/min.
Injection volume:	20 μL
UV detector:	230 nm
Retention Time:	Fenoxycarb=3.95 ± 0.2 minutes, Pyriproxyfen=7.95±0.2 minutes

For Hydramethylnon,

Instrument:	HPLC, Hewlett- Packard Model 1050, controlled by Chemstation
Column:	Pickering Column for carbamate analysis 5 μ, 4.6 mm, 25 cm long
Mobile Phase:	95% buffer A and 5% buffer B
Flow:	1.0 mL
Injection Volume:	20 μL
UV detector:	290 nm
Retention Time:	5.2±0.2 minutes

* Both instruments operate in ambient temperature. The Retention Time of each compound may shift dramatically if temperature changes too much.

Instrument Calibration:

1. Load a method, set the desired condition for analysis on both instruments.
2. Run 0.1, 0.2 1.0, 5.0 and 10 ηg/μL to check the system linearity for Hydramethylnon.
3. Run 0.05, 0.2, 1.0, 5.0 and 10 ηg/μL to check the system linearity for Fenoxycarb and Pyriproxyfen.

Analysis:

Quality Control:

1. A 5-point calibration curve of 0.1, 0.2, 1.0, 5.0 and 10 ηg/μL for Hydramethylnon and a 5-point calibration curve of 0.05, 0.2, 1.0, 5.0 and 10ηg/μL for Fenoxycarb and Pyriproxyfen were obtained at the beginning and the end of each set of samples.
2. Each sample shall be injected two times to insure reliability of the analysis. If the signal of a sample is greater than that of the highest standard in the calibration curve, dilute the sample. Re-inject the diluted sample together with standards twice more. A sample set is usually comprised of 10 samples, a blank and a spike.

Analysis: (continuous)

Method Detection Limit (MDL):

Method Detection Limit (MDL) refers to the lowest concentration of analyte that a method can detect reliably in either a sample or a blank. To determine the MDL, spike 7 samples, 500 ± 1g of background surface water each, with 0.2 ppb of Fenoxycarb, Pypripoxyfen and 0.5 ppb of Hydramethylnon and process each through the entire method along with a blank. The standard deviation derived from the 7 spike results was used to calculate the MDL using the following equation:

$$MDL = ts$$

Where: t = the student "t" value for the 99% confidence level with n-1degrees of freedom (t = 3.143 for 6 degrees of freedom). n = the number of replicates.

S = the standard deviation obtained from the 7 replicates analysis.

The results for the standard deviations and MDL are in Appendix 1: Table 1.

Reporting Limit (RL):

RL refers to level above which quantitative results may be obtained. The MDL was used as a guide to determine the RL. The reporting limit for the method is 0.1ppb for fenoxycarb, pyriproxyfen and 0.2 ppb for hydramethylnon.

Recovery Data:

Method validation was made by preparing eight sets of spike samples. Each set contained a blank and three levels of spikes. The background water (American River water) was obtained from Department of Pesticide Regulation. Each set was processed through the entire analytical method. Recoveries of Fenoxycarb, Pyriproxyfen and Hydramethlynon are shown in Appendix 1: Table 2.

Calculations:

$$ppb = \frac{(\text{sample peak ht.})(\text{response factor, } \eta g)(\text{sample final vol., mL})(1000\mu L/mL)}{(\text{sample vol. injected, } \mu L)(\text{sample wt., g})}$$

$$\text{where: response factor } (\eta g) = \frac{\Sigma[\ (\text{std. conc.}_n, \eta g/\mu L)\ (\text{std. vol. injected, } \mu L)/\ (\text{std. peak ht.}_n)]}{n}$$

n = number of standards

Discussion:

1. During our initial method validation process we encountered an extreme problem of low recovery for Hydramethylnon in two spiked samples. We examined every step for a clue to the problem. The finding was inconclusive. We decided to abandon all 5 sets of validation data and re-validated with slight modification of the method. The reported 8 sets of data are generated according to this method. It is our concern that the problem of low recovery may occur again. We will pay attention to this problem very closely.

Discussion: (continuous)

2. MDL and three sets validation for well water were done from 6/22/00 to 6/28/00. The results are in Appendix 2: Table 3 and 4. All three compounds were spiked 0.2 ηg/μL for MDL. Same spike levels for surface water were used for well water validation.

References:

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REVIEWED BY: Catherine Cooper

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Appendix 1:

Table1. Fenoxycarb, Pyriproxyfen and Hydramethylnon MDL Results (ppb) for surface water

Spike #	Fenoxycarb	Pyriproxyfen	Hydramethylnon
1	0.174	0.218	0.402
2	0.199	0.206	0.422
3	0.192	0.200	0.367
4	0.190	0.200	0.328
5	0.191	0.189	0.348
6	0.191	0.206	0.387
7	0.203	0.219	0.401
S =	0.0092	0.0107	0.0333
MDL = 3.143 x S	0.0288	0.0337	0.1045

Table 2. Fenoxycarb, Pyriproxyfen and Hydramethylnon Method Validation Results and Recovery for surface water

	Fenoxycarb		**Pyriproxyfen**		**Hydramethylnon**	
Spike Level (ppb)	Result (ppb)	Recovery (%)	Result (ppb)	Recovery (%)	Result (ppb)	Recovery (%)
1	0.965	96.5	0.994	99.4	0.705	70.5
	0.960	96.0	0.957	95.7	0.791	79.1
	0.969	96.9	0.973	97.3	0.753	75.3
	0.980	98.0	1.004	100.4	0.745	74.5
	0.958	95.8	1.017	101.7	0.759	75.9
	0.975	97.5	0.980	98.0	0.786	78.6
	0.947	94.7	0.949	94.9	0.753	75.3
	0.983	98.3	1.016	101.6	0.814	81.4
10	11.2	111.8	9.784	97.8	8.84	88.4
	9.69	96.9	9.78	97.8	9.72	97.2
	8.81	88.1	9.05	90.5	7.86	78.6
	11.0	110.0	10.89	108.9	10.75	107.5
	9.60	96.0	9.58	95.8	9.76	97.6
	9.94	99.4	9.82	98.2	10.45	104.5
	9.22	92.2	9.34	93.4	104.9	104.9
	9.79	97.9	9.81	98.1	10.81	108.1
100	90.1	90.1	98.7	98.7	71.3	71.3
	97.8	97.8	98.2	98.2	85.3	85.3
	95.2	95.2	92.8	92.8	66.8	66.8
	102.0	102.0	100.6	100.6	71.5	71.5
	101.4	101.4	100.7	100.7	87.7	87.7
	96.6	96.6	95.3	95.3	77.2	77.2
	97.5	97.5	96.1	96.1	101.9	101.9
	97.9	97.9	97.8	97.8	79.7	79.7

Appendix 2:

Table3. Fenoxycarb, Pyriproxyfen and Hydramethylnon MDL Results (ppb) for well water

Spike #	Fenoxycarb	Pyriproxyfen	Hydramethylnon
1	0.186	0.183	0.205
2	0.188	0.183	0.161
3	0.182	0.169	0.149
4	0.185	0.179	0.130
5	0.183	0.183	0.189
6	0.185	0.178	0.208
7	0.222	0.202	0.209
S =	0.0142	0.0102	0.0320
MDL = 3.143 x S	0.0447	0.0322	0.1006

Table 4. Fenoxycarb, Pyriproxyfen and Hydramethylnon Method Validation Results and Recovery for well water

	Fenoxycarb		**Pyriproxyfen**		**Hydramethylnon**	
Spike Level (ppb)	Result (ppb)	Recovery (%)	Result (ppb)	Recovery (%)	Result (ppb)	Recovery (%)
1	0.975	97.5	0.950	95.0	0.887	88.7
	0.708	70.8	0.941	94.1	0.717	71.7
	1.024	102.4	1.013	101.3	0.764	76.4
10	8.368	83.7	8.687	86.9	8.349	83.5
	8.994	89.9	9.280	92.8	7.910	79.1
	12.199	122.0	12.459	124.6	11.472	114.7
100	86.326	86.3	89.143	89.1	80.013	80.0
	93.030	93.0	98.200	98.2	79.531	79.5
	88.623	88.6	89.567	89.6	75.485	75.5

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Method #: EM 46.0
Original Date:12/19/95
Revised: 05/01/97

Determination of Organophosphate Pesticides in Surface Water using Gas Chromatography

Scope: This method is for the determination of organophosphate pesticides in surface water. The reporting limit (RL) of the method for diazinon and chlorpyrifos is 0.04 µg/L. Dichlorvos (DDVP), dimethoate, methyl parathion, malathion, ethyl parathion, methidation, phosmet, phosalone, azinphos-methyl, thimet, ethoprop and fonofos have a RL of 0.05 µg/L.

Principle: The surface water sample is extracted with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated to dryness on a rotary evaporator and diluted to a final volume of 1.0 mL with acetone. The extract is then analyzed using a gas chromatograph equipped with a flame photometric detector (FPD).

Reagents, Equipment and Instruments:

Reagents:

1. Methylene Chloride (pesticide residue grade)
2. Acetone (pesticide residue grade)
3. Sodium sulfate, anhydrous
4. Organophosphate pesticide stock standard solutions (1mg/mL): Obtain standards from Center for Analytical Chemistry, CDFA

Equipment:

1. Rotary evaporator (Büchi/Brinkmann)
2. Nitrogen evaporator (Organomation Model # 112)
3. Vortex-vibrating mixer
4. Conical test tube with glass stopper, 15 mL, graduated
5. Separatory funnel, 2 L
6. Boiling flask, 500 mL
7. Whatman filter paper, #4, 15 cm
8. Funnel, long stem, 60°, 100 mm
9. Disposable Pasteur pipettes, 5.75 inches
10. Balance (Mettler PC 4400)

Instrument:

Hewlett Packard 5890 Series II GC with FPD and a HP-1, methyl silicone gum megabore column(10 m x 0.53 mm x 2.65 µm).

Analysis:

Sample Extraction:

1. Remove water samples from refrigerator and allow them to come to room temperature.
2. Record weight of water by weighing sample bottle before and after water has been transferred into a separatory funnel.
3. Extract sample by shaking with 100 mL of methylene chloride for 2 minutes. ***Vent frequently to relieve pressure.***
4. After the phases have separated, drain the lower methylene chloride layer through 20 g of anhydrous sodium sulfate, into a boiling flask.
5. Repeat steps 3 & 4 two more times using 80 mL of methylene chloride each time.
6. After draining the final extraction, rinse the sodium sulfate with 25 mL of methylene chloride.
7. Evaporate the sample extract to just dryness on a rotary evaporator using a 35 °C water bath and approximately 20 inches Hg vacuum.
8. Add 5 mL of acetone and swirl to dissolve the residue in the flask. Transfer the extract to a calibrated 15-mL graduated test tube.
9. Rinse flask 2 more times, each time with 2 mL of acetone and transfer each rinse to the same test tube.
10. Under a gentle stream of nitrogen with no heat applied, evaporate the extract to a volume slightly less than 1 mL. Then, bring to a final volume of 1.0 mL with acetone.
11. Submit extract for GC analysis.

Instrument Conditions

Primary Analysis:

Instrument: Hewlett Packard 5890 Series II GC with FPD
Column: HP-1, methyl silicone gum, 10 m x 0.53 mm x 2.65 µm
Carrier gas: helium, column flow rate 20 mL/min.
Injector temperature: 220 °C
Detector temperature: 250 °C
Injection volume: 3 µL
Column oven temperature:

Initial temperature:	150 °C held for 1 minute
Ramp rate 1:	10 °C/min.
Final temperature:	200 °C held for 2 minutes
Ramp rate 2:	20 °C/min.
Final temperature:	250 °C held for 5 minutes

Confirmation Analysis:

Instrument: Hewlett Packard 5890 Series II GC with FPD
Column: HP-17, 50% phenyl methyl silicone gum, 10 m x 0.53 mm x 2.0µm
Injector temperature: 220 °C
Detector temperature: 250 °C
Injection volume: 3 µL
Column oven temperature:
Same as primary analysis conditions.

Analysis: continued

	Retention times:	
Chemicals	HP-1	HP-17
DDVP	0.68	1.10
Dimethoate	3.25	6.22
Diazinon	4.10	5.36
Methyl Parathion	4.75	7.50
Malathion	5.51	8.21
Chlorpyrifos	5.75	7.93
Methidathion	6.67	10.36
Phosmet	10.16	13.71
Azinphos-Methyl	10.72	15.14
Ethoprop	2.67	3.96
Thimet	3.16	4.56
Fonofos	3.89	5.62
Ethyl parathion	5.70	8.38
Phosalone	10.81	13.49

Calculations:

$$\mu g/L = \frac{\text{(peak ht of sample) (std. conc.) (std. vol. injected) (final vol. sample, mL) (1000 } \mu L/mL)}{\text{(peak ht. std) (sample vol. injected) (sample wt., g)}}$$

Method Performance:

Quality Control:

A three point calibration curve (0.04 ng/μL, 0.08 ng/μL and 0.2 ng/μL) was obtained at the beginning and the end of each set of samples. Each samples shall be injected two times to insure reliability of the analysis. If a sample signal is greater than the highest standard, dilute the sample. Reinject the diluted sample and standards twice more.

Recovery Data:

Method validation was made by spiking 1000 g of American River water with five different levels of spikes (0.08, 0.2, 0.5, 1.0, and 5.0 μg/L) and a blank for five different days (see appendix I). Recoveries of the analytes are summarized below:

Recovery of Organophosphate Pesticides in Surface Water

Organophosphate Pesticides	Spike level (μg/L)	# Spike (n)	Mean Recovery (%)	Standard Deviation (Based on % Recovery)
DDVP	0.08	5	90.5	6.94
	0.2	5	90.3	6.19
	0.5	5	85.0	10.4
	1.0	5	82.9	3.83
	5.0	5	87.6	8.64

Method Performance: continued

Organophosphate Pesticides	Spike level (µg/L)	# Spike (n)	Mean Recovery (%)	Standard Deviation (Based on % Recovery)
Dimethoate	0.08	5	102	3.14
	0.2.	5	98.0	9.15
	0.5	5	103	5.11
	1.0	5	96.9	9.03
	5.0	5	96.2	5.58
Diazinon	0.08	5	95.5	5.77
	0.2	5	88.4	8.86
	0.5	5	90.7	4.40
	1.0	5	85.9	4.55
	5.0	5	89.6	4.24
Methyl Parathion	0.08	5	97.8	9.50
	0.2	5	101	8.62
	0.5	5	97.8	6.16
	1.0	5	93.7	4.36
	5.0	5	94.0	5.44
Malathion	0.08	5	96.3	8.79
	0.2	5	95.1	9.67
	0.5	5	95.4	3.25
	1.0	5	92.0	4.41
	5.0	5	94.3	3.83
Ethyl parathion	0.08	5	101	13.5
	0.2	5	97.0	4.65
	0.5	5	91.0	6.82
	1.0	5	93.7	8.55
	5.0	5	93.2	5.52
Chlorpyrifos	0.08	5	95.8	7.58
	0.2	5	96.7	9.39
	0.5	5	93.8	1.67
	1.0	5	90.8	6.18
	5.0	5	92.6	2.71
Methidathion	0.08	5	102	7.23
	0.2	5	104	9.50
	0.5	5	93.0	2.26
	1.0	5	96.1	5.66
	5.0	5	95.4	4.49

Method Performance: continued

Organophosphate Pesticides	Spike level (µg/L)	# Spike (n)	Mean Recovery (%)	Standard Deviation (Based on % Recovery)
Phosmet	0.08	5	95.8	8.13
	0.2	5	103	8.36
	0.5	5	97.2	3.64
	1.0	5	99.9	9.30
	5.0	5	97.3	4.66
Azinphos-Methyl	0.08	5	96.0	2.05
	0.2	5	103	7.55
	0.5	5	98.2	4.32
	1.0	5	110	6.03
	5.0	5	98.4	3.20
Phosalone	0.08	5	98.3	4.42
	0.2	5	103	6.96
	0.5	5	92.4	5.65
	1.0	5	102	5.89
	5.0	5	101	5.30
Thimet	0.08	5	90.0	7.86
	0.2	5	83.6	5.19
	0.5	5	82.7	4.12
	1.0	5	86.7	9.07
	5.0	5	82.9	9.45
Ethoprop	0.08	5	92.8	7.26
	0.2	5	89.9	6.69
	0.5	5	88.9	4.13
	1.0	5	90.6	10.1
	5.0	5	92.5	6.15
Fonofos	0.08	5	91.0	10.1
	0.2	5	89.4	5.59
	0.5	5	85.2	4.28
	1.0	5	86.7	9.81
	5.0	5	89.7	7.09

Method Performance: continued

Method Detection Limit:

Data used to calculated the method detection limit (MDL) is in appendix II. The MDL is as follows:

Compound	STDEV (µg/L)	MDL (µg/L)
DDVP	0.003	0.009
Ethoprop	0.005	0.016
Dimethoate	0.003	0.009
Thimet	0.005	0.016
Fonofos	0.004	0.013
Diazinon	0.003	0.009
M. Parathion	0.003	0.009
Malathion	0.004	0.013
E. Parathion	0.003	0.009
Chlorpyrifos	0.004	0.013
Methidathion	0.008	0.025
Phosmet	0.004	0.013
Azinphos methyl	0.008	0.025
Phosalone	0.004	0.013

These are the minimum concentrations of the above compounds that can be reported with 99% confidence. The method detection limit (MDL) was computed based on the following procedure:
a) Prepared 7 replicates of the analytes at 0.05 µg/L using American River water.
b) Compute the MDL as follows:

$$\mathbf{MDL} = t \times S$$

where;
t is the Student 't' value for the 99% confidence level with n-1 degrees of freedom (n-1, 1 - α = 0.99). n represents the number of replicates.
S denotes the standard deviation obtained from replicate analyses.

Reporting Limit

The reporting limits (RL) for diazinon and chlorpyrifos are 0.04 µg/L. For the remaining compounds, the RL is 0.05 µg/L. The MDL is used as a guide to determine the RL for this method. The RL is 1 - 5 times the MDL.

Discussion:

Methidathion, phosmet, azinphos methyl and phosalone compounds were enhanced by the matrix used in the validation. To eliminate the matrix problem, spike samples at level of 0.08, 0.2 and 0.5 ppb were calculated using standards prepared in blank matrix extract. The 0.08 and 0.2 µg/mL standards were prepared by pipetting 1 mL of background matrix into different test tubes and evaporating them to dryness in a nitrogen evaporator at 40 °C. Then, 1 ml of the working

Discussion: continued

standard was pipetted into the test tube separately and mixed well. These standards were used to calculate the 0.08 and 0.2 µg/L spikes. The 0.5 µg/mL standard was prepared by pipetting 0.2 mL of background matrix extract into a test tube and evaporating it to dryness in a nitrogen evaporator at 40 °C. Then, 1 mL of 0.5 µg/mL working standard was pipetted into the test tube and mixed well. This standard was used to calculate the 0.5 µg/L spikes. The 1.0 and 5.0 µg/L spikes were calculated using standards without addition of background matrix extract.

Several peaks were noted in the chromatograms of the blank and samples that had the same retention times as those of phosmet, phosalone and azinphos-methyl. These interferences may have been caused by impurities in the sodium sulfate used. The interfering peaks disappeared after the sodium sulfate used in extraction had been washed with methylene chloride. To avoid these interferences, it is recommended that the sodium sulfate should be washed with methylene chloride prior to use.

Reference:

1. *SOP QAQC001.0*, California Department of Pesticide Regulation, Environmental Hazards Assessment Program, 1995.

2. *Method 8141, Organophosphorus Pesticides, Capillary Column*. EPA Test Methods for Evaluating Solid Waste. Revised Methods, 1987.

3. *EPA Method 507, Pesticides, Capillary Column*. EPA Test Method for Drinking water and raw source water, 1987.

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Appendix I

Day 1 - OP's Method Validation						
	Results in ug/L					
Analyte	Blank	0.08 ng/uL	0.2 ng/uL	0.5 ng/uL	1.0 ng/uL	5.0 ng/uL
DDVP	ND	0.064	0.164	0.437	0.817	4.57
Cygon	ND	0.085	0.201	0.527	0.918	4.88
Diazinon	ND	0.072	0.164	0.459	0.830	4.69
M. Parathion	ND	0.085	0.209	0.541	0.970	5.12
Malathion	ND	0.074	0.180	0.482	0.860	4.80
Dursban	ND	0.072	0.178	0.467	0.816	4.66
Supracide	ND	0.082	0.208	0.475	0.892	4.67
Imidan	ND	0.073	0.215	0.485	0.861	5.20
Guthion	ND	0.076	0.203	0.502	1.07	4.79
Ethoprop	ND	0.078	0.200	0.447	1.00	4.88
Timet	ND	0.074	0.184	0.394	0.938	4.63
Fonofos	ND	0.075	0.194	0.409	0.959	4.75
E. Parathion	ND	0.080	0.204	0.425	1.02	4.92
Zolone	ND	0.072	0.225	0.413	1.01	5.21
Day 2 - OP's Method Validation						
	Results in ug/L					
Analyte	Blank	0.08 ng/uL	0.2 ng/uL	0.5 ng/uL	1.0 ng/uL	5.0 ng/uL
DDVP	ND	0.079	0.198	0.500	0.879	5.01
Cygon	ND	0.080	0.169	0.544	1.09	5.22
Diazinon	ND	0.080	0.198	0.487	0.937	4.68
M. Parathion	ND	0.084	0.211	0.490	0.959	4.79
Malathion	ND	0.085	0.207	0.499	0.972	4.86
Dursban	ND	0.085	0.212	0.480	0.921	4.61
Supracide	ND	0.091	0.232	0.467	1.03	5.10
Imidan	ND	0.072	0.196	0.466	1.09	4.99
Guthion	ND	0.075	0.208	0.519	1.15	5.08
Ethoprop	ND	0.073	0.186	0.433	0.768	4.12
Timet	ND	0.069	0.168	0.411	0.710	3.83
Fonofos	ND	0.069	0.186	0.420	0.701	3.98
E. Parathion	ND	0.072	0.187	0.430	0.803	4.21
Zolone	ND	0.073	0.195	0.470	0.932	4.68

Appendix I (cont)

Day 3 - OP's Method Validation						
	Results in ug/L					
Analyte	Blank	0.08 ng/uL	0.2 ng/uL	0.5 ng/uL	1.0 ng/uL	5.0 ng/uL
DDVP	ND	0.075	0.177	0.422	0.783	4.07
Cygon	ND	0.080	0.205	0.477	0.851	4.64
Diazinon	ND	0.078	0.187	0.447	0.824	4.41
M. Parathion	ND	0.079	0.203	0.466	0.863	4.55
Malathion	ND	0.082	0.202	0.482	0.895	4.77
Dursban	ND	0.080	0.206	0.472	0.878	4.83
Supracide	ND	0.080	0.196	0.474	0.913	4.83
Imidan	ND	0.079	0.183	0.490	0.962	4.85
Guthion	ND	0.079	0.209	0.464	1.01	4.71
Ethoprop	ND	0.065	0.166	0.416	0.848	4.61
Timet	ND	0.066	0.165	0.393	0.876	3.53
Fonofos	ND	0.066	0.172	0.404	0.898	4.52
E. Parathion	ND	0.071	0.185	0.448	0.927	4.63
Zolone	ND	0.074	0.213	0.484	1.07	4.87
Day 4 - OP's Method Validation						
	Results in ug/L					
Analyte	Blank	0.08 ng/uL	0.2 ng/uL	0.5 ng/uL	1.0 ng/uL	5.0 ng/uL
DDVP	ND	0.073	0.179	0.409	0.811	3.91
Cygon	ND	0.079	0.188	0.517	1.02	4.49
Diazinon	ND	0.081	0.154	0.447	0.847	4.18
M. Parathion	ND	0.066	0.171	0.467	0.933	4.41
Malathion	ND	0.067	0.161	0.457	0.923	4.38
Dursban	ND	0.070	0.169	0.457	0.961	4.45
Supracide	ND	0.075	0.183	0.447	0.984	4.49
Imidan	ND	0.087	0.213	0.514	1.01	4.66
Guthion	ND	0.076	0.183	0.494	1.16	4.98
Ethoprop	ND	0.075	0.174	0.457	1.00	4.66
Timet	ND	0.082	0.163	0.432	0.898	4.18
Fonofos	ND	0.086	0.176	0.446	0.905	4.31
E. Parathion	ND	0.098	0.204	0.510	1.01	4.69
Zolone	ND	0.075	0.201	0.477	1.08	5.29

Appendix I (cont)

Day 5 - OP's Method Validation						
	Results in ug/L					
Analyte	Blank	0.08 ng/uL	0.2 ng/uL	0.5 ng/uL	1.0 ng/uL	5.0 ng/uL
DDVP	ND	0.071	0.185	0.356	0.857	4.34
Cygon	ND	0.083	0.217	0.501	0.974	4.83
Diazinon	ND	0.071	0.181	0.427	0.859	4.45
M. Parathion	ND	0.077	0.212	0.480	0.960	4.61
Malathion	ND	0.077	0.201	0.466	0.949	4.75
Dursban	ND	0.076	0.202	0.469	0.962	4.62
Supracide	ND	0.082	0.218	0.463	0.985	4.76
Imidan	ND	0.072	0.225	0.475	1.08	4.65
Guthion	ND	0.078	0.225	0.476	1.10	5.03
Ethoprop	ND	0.080	0.173	0.469	0.911	4.86
Timet	ND	0.069	0.156	0.437	0.914	4.56
Fonofos	ND	0.068	0.166	0.451	0.874	4.87
E. Parathion	ND	0.081	0.190	0.462	0.934	4.84
Zolone	ND	0.081	0.191	0.466	1.01	5.21

Apendix II

MDL - OP's Method											
	Results in ppb										
Analyte	Blank	Spk 1	Spk 2	Spk 3	Spk 4	Spk 5	Spk 6	Spk 7	STDEV	MDL (ug/L)	RL (ug/L)
DDVP	0.000	0.040	0.035	0.046	0.040	0.040	0.042	0.039	0.003	0.009	0.05
ETHOPROP	0.000	0.043	0.049	0.036	0.043	0.051	0.043	0.047	0.005	0.016	0.05
CYGON	0.000	0.053	0.050	0.052	0.047	0.046	0.050	0.047	0.003	0.009	0.05
TIMET	0.000	0.038	0.050	0.038	0.044	0.049	0.041	0.047	0.005	0.016	0.05
FONOFOS	0.000	0.040	0.044	0.036	0.043	0.049	0.044	0.046	0.004	0.013	0.05
DIAZINON	0.000	0.052	0.044	0.050	0.045	0.043	0.047	0.045	0.003	0.009	0.04
M. PARATHION	0.000	0.053	0.048	0.046	0.046	0.045	0.050	0.044	0.003	0.009	0.05
MALATION	0.000	0.054	0.048	0.051	0.044	0.043	0.049	0.044	0.004	0.013	0.05
E. PARATHION	0.000	0.046	0.052	0.045	0.047	0.052	0.048	0.049	0.003	0.009	0.05
DURSBAN	0.000	0.052	0.046	0.051	0.043	0.042	0.050	0.043	0.004	0.013	0.04
SUPRACIDE	0.000	0.069	0.052	0.055	0.049	0.046	0.052	0.045	0.008	0.025	0.05
IMIDAN	0.000	0.079	0.073	0.080	0.073	0.068	0.071	0.071	0.004	0.013	0.05
GUTHION	0.000	0.071	0.061	0.078	0.061	0.058	0.057	0.056	0.008	0.025	0.05
ZOLONE	0.000	0.044	0.052	0.052	0.050	0.056	0.055	0.056	0.004	0.013	0.05

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Revision:
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Title: Determination of Organophosphate Pesticides in Surface water using Gas Chromatography

1. Scope:

   This section method (SM) documents the selected organophosphate pesticides analysis in surface water by all authorized section personnel.

2. Principle:

   The surface water sample is extracted with methylene chloride. The extract is passed through sodium sulfate to remove residual water. The anhydrous extract is evaporated to almost dryness on a rotary evaporator and diluted to a final volume of 1.0 mL with acetone. The extract is then analyzed by a gas chromatograph equipped with flame photometric detector (FPD) and any positive result is confirmed by mass selective detector (MSD).

3. Safety:

   3.1 All general laboratory safety rules for sample preparation and analysis shall be followed.

   3.2 Methylene chloride is a regulated and controlled carcinogenic hazardous substance. It must be stored and handled in accordance with California Code of Regulations, Title 8, Subchapter 7, Group 16, Article 110, Section 5202.

   3.3 All solvents should be handled with care in a ventilated area.

4. Interferences:

   There are matrix interferences that cause quantitative problems. Therefore the calibration standards will be made up in appropriate matrix.

5. Apparatus and Equipment:

   5.1 Rotary evaporator (Büchi/Brinkman or equivalent)
   5.2 Nitrogen evaporator (Meyer N-EVAP Organomation Model # 112 or equivalent)
   5.3 Vortex-vibrating mixer
   5.4 Balance (Mettler PC 4400) or equivalent

5.5 Gas Chromatograph equipped with a flame photometric detector (FPD) in phosphorus mode
5.6 Gas Chromatograph equipped with mass selective detector(MSD)

6. Reagents and Supplies

6.1	Methylene Chloride, nanograde or equivalent pesticide grade	
6.2	Acetone, nanograde or equivalent pesticide grade	
6.3	Anhydrous Sodium Sulfate, granular	
6.4	Ethoprophos	CAS# 13194-48-4
6.5	Diazinon	CAS# 333-41-5
6.6	Disulfoton	CAS# 298-04-4
6.7	Chlorpyrifos	CAS# 2921-88-2
6.8	Malathion	CAS# 121-75-5
6.9	Methidation	CAS# 950-37-8
6.10	Fenamiphos	CAS# 22224-92-6
6.11	Azinphos Methyl	CAS# 86-50-0
6.12	Dichlorvos	CAS# 62-73-7
6.13	Phorate	CAS# 298-02-2
6.14	Fonofos	CAS# 66767-39-3
6.15	Dimethoate	CAS# 60-51-5
6.16	Parathion methyl	CAS# 298-00-0
6.17	Tribufos (DEF)	CAS# 13071-79-9
6.18	Profenofos	CAS# 41198-08-7

6.19 Conical tube with glass stopper, 15-mL graduated, 0.1 mL subdivision
6.20 Separatory funnel, 2 L
6.21 Boiling flask, 500 mL
6.22 Whatman filter paper, #4, 15 cm
6.23 Funnel, long stem, 10 mm diameter
6.24 Disposable Pasteur pipettes, and other laboratory ware as needed
6.25 Recommended analytical columns:

For FPD – Restek's Rtx® - OPPesticides (fused silica column), 30 m x 0.25 mm x 0.4 μm film thickness or 30 m x 0.32 mm x 0.5 μm film thickness, and Rtx® - OPPesticides2 (fused silica column), 30 m x 0.25 mm x 0.25 μm film thickness or 30 m x 0.32 mm x 0.32 μm film thickness.

For MSD - 5% phenyl Methylsilicone (HP-5ms or equivalent) fused silica column, 30 m x 0.25 mm x 0.25 μm film thickness.

7. Standards Preparation:

   7.1 Dilute the 1 mg/mL Organophosphate standards obtained from the CDFA/CAC Standards Repository with acetone to make up a series of mixed working standards(see 10.2). These standards shall be prepared to cover the linear range from 0.025 ηg/μL to 0.5 ηg/μL.

   7.2 The calibration standards are added to matrix blank extracts (9.1.2.1) to correct for matrix background interference.

   7.3 Keep all standards in designated refrigerator for storage.

   7.4 The expiration date of each mixed working standard is six months from the preparation date.

8. Sample Preservation and Storage:

   All water samples and sample extracts shall be stored in the refrigerator (32-40 ^{o}F).

9. Test Sample Preparation:

   9.1 Sample Preparation

      9.1.1 Remove samples from refrigerator and allow samples to come to room temperature before extraction.

      9.1.2 Preparation of matrix blank and matrix spike:

         The Department of Pesticide Regulations (DPR) provide the background water for matrix blank and spikes.

         9.1.2.1 Matrix blank: Weigh out 1000 g of background water and follow the test sample extraction procedure.

         9.1.2.2 Matrix spike: Weigh out 1000 g of background water. Spike a client requested amount of organophosphate pesticides into the background water and let it stand for 1 minute. Follow the test sample extraction procedure.

9.2 Test Sample Extraction

9.2.1 Record the weight of water by subtracting the weight of the sample container before and after water has been transferred into a separatory funnel.

9.2.2 Shake with 100 mL of methylene chloride for 2 minutes. Vent frequently to relieve pressure.

9.2.3 After phases have separated, drain lower methylene chloride layer through 20 g of anhydrous sodium sulfate, into a 500 mL boiling flask.

9.2.4 Repeat steps 9.2.2 & 9.2.3 two more times using 80 mL of methylene chloride each time. Combine the extracts in the same boiling flask.

9.2.5 After draining the final extraction, rinse the sodium sulfate with 25 mL of methylene chloride.

9.2.6 Evaporate the sample extract to ~ 3 mL on a rotary evaporator using a water bath at ~ 35 °C and ~ 15 - 20 inch Hg vacuum. Add ~ 3 mL of acetone and rotoevaporate to 1 - 2 mL. Transfer the extract to a calibrated 15 mL graduated test tube.

9.2.7 Rinse flask 3 more times with 3 mL of acetone and transfer each rinse to the same test tube.

9.2.8 Evaporate the extract to a volume slightly less than 1 mL in a water bath at 25 to 35 ° C under a gentle stream of nitrogen. Then bring to a final volume of 1 mL with acetone, mix well and transfer into two autosampler vials.

9.2.9 Submit extract for GC analysis.

10. Instrument Calibration:

10.1 The calibration standards are added to a matrix blank extract to correct for matrix background interference.

10.2 A calibration standard curve consists of minimum of three levels. The concentration of 0.025, 0.05, 0.1, 0.25, 0.5 or 1.0 ηg/µL standards are recommended. Calibration is obtained using a linear or quadratic regression with the correlation coefficient (r) equal to or greater than 0.995.

10.3 Suggested composition of calibration mixed standards are as follow.

OP-1 Mixed Standard	**OP-2 Mixed Standard**
Ethoprophos	Dichlorvos
Diazinon	Phorate
Disulfoton	Fonofos
Chlorpyifos	Dimethoate
Malathion	Parthion-methyl
Methidathion	DEF
Fenamiphos	Profenofos
Azinphos-methyl	

11. Analysis:

11.1 Injection Scheme

Follow the sequence of Solvent, Calibration standards, Solvent, Matrix Bank, Matrix Spike, Test Samples (maximum of 10-12 samples) and Calibration standards. Inject an old sample or matrix blank before the sequence analysis to condition the instrument is recommended.

11.2 GC Instrumentation

11.2.1 Analyze OP pesticides by a gas chromatograph equipped with two flame photometric detectors and two different columns.

11.2.2 Recommended instrument (GC/FPD) parameters: Injector 250 °C; detector 250 °C; oven temperature 80 °C (hold 2 min.) to 180 °C @ 20 °C/min. to 280 °C @ 6 °C/min. (hold 6 min.); injection volume 4 µL.

11.2.3 Confirm OP pesticides by a gas chromatograph equipped with mass selective detector.

11.2.4 Recommended instrument (GC/MSD) parameters: Injector 250 °C; MSD transfer line heater 280 °C; oven temperature 70 °C (hold 1 min.) to 190 °C @ 15 °C/min.(hold 2 min.) to 250 °C@ 15 °C/min. (hold 6 min.); injection volume 4 µL.

12. Quality Control:

12.1 Each set of samples shall have a matrix blank and minimum of one matrix spike sample.

12.2 The matrix blank shall be free of target compounds.

12.3 The recoveries of the matrix spike should be within the control limits.

12.4 The retention time shall be within ± 2 per cent of that of the standard.

12.5 The sample must be diluted if results fall outside the linear range of the standard curve.

12.6 Bracketing standard curves should have a percent change less than 15 % for most of organophosphate compounds, and 20 – 25 % for late eluted OP compounds.

12.7 Method Detection Limits (MDL)

The method detection limit refers to the lowest concentration of analyte that a method can detect reliably. To determine the MDL, 7 replicate water samples are spiked at 0.05 ppb. The standard deviation from the spiked sample recoveries are used to calculate the MDL for each analyte using the follow equation:

$$MDL = tS$$

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicate used to determine the MDL, t=3.143.

12.8 Reporting limit (RL):

The reporting limit (RL) refers to the level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. Agreed upon per client agreement, the RL is chosen in a range 1-5 times the MDL.

MDL data and the RL are tabulated in Appendix I.

12.9 Method Validation Recovery Data and Control Limits:

12.9.1 The method validation consisted of five samples sets. Each set included seven levels of fortification (0.05, 0.1, 0.25, 0.5, 1.0, 2.0, and 5.0 ppb) and a method blank. All spikes and method blank samples were processed through the entire analytical method.

12.9.2 Upper and lower warning and control limits are set at ± 2 and 3 standard deviations of the average % recovery, respectively.

Method validation results and control limits are tabulated in Appendix II.

13. Calculations:

Quantitation is based on external standard (ESTD) calculation using either the peak area or height. The software uses a linear or quadratic curve fit, with all levels weighted equally. Alternatively, at chemist discretion, concentrations may be calculated using the response factor for the standard whose value is closest to the level in the sample.

$$ppb = \frac{(\text{sample peak ht. or area})(\text{std. conc.})(\text{std. vol. injected})(\text{sample final vol., (mL)})(1000\ \mu L/mL)}{(\text{std. peak ht. or area})(\text{sample vol. injected})(\text{sample wt., g})}$$

14. Reporting Procedure:

14.1 Identification of Analyte

For responses within calibration range, compare the retention time of the peaks with the retention time of standards. For positive results retention times shall not vary from the standards more than 2 percent.

14.2 The Restek's Rtx® - OPPesticides column is used as the primary analytical column, the 2nd column, Rtx® - OPPesticides2 column and GC/MSD used as confirmation.

Sample results and the data reported in the Appendix I and II were calculated from the Rtx® - OPPesticides column.

14.3 Sample results are reported out according to the client's analytical laboratory specification sheet.

15. Discussion and References:

15.1 Sample response and quantitation vary depending on matrix background in the samples. The calibration standards were added to a matrix blank extract to correct for matrix background interference.

15.2 Two different sizes of analytical column (ID of 0.25 and 0.32 mm) were used in this method. The column with larger ID (0.32 mm) seems to give more reproducible results, since 4 μL sample extract was injected.

The retention times for OP pesticides are tabulated in Appendix III.

15.3 Some of the late eluting compounds were observed to suffer gradual losses in sensitivity. We recommend changing the injector liner and trimming the column when this occurs.

16. References:

16.1 *EPA Method 507, Pesticides, Capillary Column.* EPA Test Method for Drinking Water and Raw Source Water, 1987.

16.2 Hsu, J. and Hernandez J. *Determination of Organophosphate Pesticides in Surface Water using Gas Chromatography*, 1997, Environmental Monitoring Method, Center for Analytical Chemistry, CDFA.

APPENDIX I

The determination of Method Detection Limit (MDL) data and Reporting Limit (RL)

Spk \ Analyte	**Ethoprophos**	**Diazinon**	**Disulfoton**	**Chlorpyrofos**	**Malathion**
0.05 ppb spk1	0.0503	0.0580	0.0528	0.0573	0.0602
0.05 ppb spk2	0.0500	0.0561	0.0513	0.0552	0.0581
0.05 ppb spk3	0.0482	0.0524	0.0490	0.0534	0.0555
0.05 ppb spk4	0.0538	0.0582	0.0525	0.0616	0.0657
0.05 ppb spk5	0.0498	0.0548	0.0514	0.0574	0.0600
0.05 ppb spk6	0.0559	0.0593	0.0569	0.0617	0.0630
0.05 ppb spk7	0.0469	0.0496	0.0477	0.0534	0.0558
SD	0.00313	0.00349	0.00296	0.00348	0.00371
MDL	0.0098	0.0110	0.0093	0.0109	0.0117
RL	0.050	0.040	0.040	0.040	0.050

Spk \ Analyte	**Methidathion**	**Fenamiphos**	**Dichlorvos**	**Phorate**	**Fonofos**
0.05 ppb spk1	0.0576	0.0610	0.0417	0.0458	0.0476
0.05 ppb spk2	0.0574	0.0585	0.0476	0.0468	0.0486
0.05 ppb spk3	0.0540	0.0587	0.0461	0.0474	0.0493
0.05 ppb spk4	0.0643	0.0683	0.0393	0.0404	0.0430
0.05 ppb spk5	0.0613	0.0638	0.0398	0.0459	0.0485
0.05 ppb spk6	0.0628	0.0674	0.0422	0.0429	0.0451
0.05 ppb spk7	0.0599	0.0608	0.0416	0.0476	0.0503
SD	0.00355	0.00397	0.00311	0.00266	0.00256
MDL	0.0111	0.0125	0.0098	0.0083	0.0080
RL	0.050	0.050	0.050	0.050	0.040

Spk \ Analyte	**Dimethoate**	**Propenofos**	**DEF**	**Parathion Methyl**	**Azinophos Methyl**
0.05 ppb spk1	0.0502	0.0538	0.0558	0.0495	0.0612
0.05 ppb spk2	0.0502	0.0541	0.0555	0.0503	0.0606
0.05 ppb spk3	0.0495	0.0526	0.0544	0.0501	0.0621
0.05 ppb spk4	0.0468	0.0519	0.0520	0.0464	0.0678
0.05 ppb spk5	0.0472	0.0535	0.0576	0.0499	0.0631
0.05 ppb spk6	0.0431	0.0440	0.0448	0.0440	0.0671
0.05 ppb spk7	0.0486	0.0545	0.0579	0.0509	0.0598
SD	0.00253	0.00371	0.00452	0.00254	0.00316
MDL	0.0079	0.0114	0.0142	0.0080	0.0099
RL	0.050	0.050	0.050	0.030	0.050

All concentrations are expressed in ppb.

APPENDIX II

Method Validation Data and Control Limit

Analyte	Spike ppb	Recovery (%) Set 1	Set 2	Set 3	Set 4	Set 5	%
Ethoprop	0.05	95.6	64.2	100.0	79.0	91.8	Mean: 91.6
	0.10	88.0	76.1	100.5	94.6	88.4	SD: 10.48
	0.25	84.8	90.8	86.0	90.0	82.0	
	0.50	91.2	88.0	100.6	84.0	84.8	UCL: 123.0
	1.0	83.7	82.6	87.9	76.2	96.7	UWL: 112.6
	2.0	107.2	103.9	95.6	91.6	90.8	LWL: 70.7
	5.0	113.1	108.9	97.2	107.6	103.2	LCL: 60.2
Diazinon	0.05	100.8	69.2	104.0	85.2	96.2	Mean: 96.6
	0.10	173.0	80.0	102.3	95.3	90.7	SD: 16.83
	0.25	90.0	94.0	88.0	91.2	84.0	
	0.50	93.4	89.8	100.8	88.6	87.2	UCL: 147.0
	1.0	85.4	87.2	88.1	79.9	97.9	UWL: 130.2
	2.0	106.5	104.4	96.7	92.1	92.6	LWL: 62.9
	5.0	109.4	123.5	98.3	113.6	100.1	LCL: 46.1
Disulfoton	0.05	95.2	58.8	92.4	80.2	83.0	Mean: 88.3
	0.10	88.0	70.5	96.7	92.3	82.2	SD: 10.09
	0.25	87.2	87.2	84.0	76.4	84.7	
	0.50	91.6	82.6	98.0	78.8	80.0	UCL: 118.6
	1.0	83.9	82.5	83.6	75.3	92.0	UWL: 108.5
	2.0	100.1	100.7	94.3	87.6	90.0	LWL: 68.1
	5.0	103.8	103.7	96.2	106.8	96.4	LCL: 58.0
Chlorpurifos	0.05	95.6	69.0	102.0	90.2	94.2	Mean: 94.5
	0.10	92.5	83.1	101.5	97.1	91.1	SD: 8.84
	0.25	92.4	95.2	88.4	90.0	116.4	
	0.50	95.0	89.4	99.6	91.6	86.4	UCL: 121.1
	1.0	86.0	91.9	87.6	81.7	97.7	UWL: 112.2
	2.0	102.8	101.2	96.3	90.1	91.2	LWL: 76.9
	5.0	105.8	107.5	98.1	111.4	98.7	LCL: 68.0

APPENDIX II (Continued)

Method Validation Data and Control Limit

Analyte	Spike ppb	Recovery (%) Set 1	Set 2	Set 3	Set 4	Set 5	%
Malathion	0.05	97.4	66.4	102.2	88.2	95.2	Mean: 95.7
	0.10	91.1	86.4	100.6	94.4	91.8	SD: 10.01
	0.25	92.8	97.6	90.0	86.8	84.0	
	0.50	95.4	91.0	1002	95.4	88.6	UCL: 125.7
	1.0	85.8	91.5	86.8	87.7	96.3	UWL: 115.7
	2.0	109.4	110.5	101.0	96.1	96.3	LWL: 75.7
	5.0	114.	112.6	102.5	117.8	105.0	LCL: 65.7
Methidathion	0.05	101.0	66.2	103.6	89.0	93.4	Mean: 95.9
	0.10	91.8	84.3	101.3	94.4	93.0	SD: 10.65
	0.25	92.0	89.6	88.8	84.0	84.8	
	0.50	93.0	89.4	99.6	95.0	89.8	UCL: 127.8
	1.0	84.9	93.0	86.0	93.3	96.7	UWL: 117.2
	2.0	111.1	111.3	102.0	97.3	96.8	LWL: 74.6
	5.0	116.4	113.7	106.0	118.6	104.4	LCL: 63.9
Fenamiphos	0.05	99.4	67.8	104.0	93.6	90.4	Mean: 96.2
	0.10	90.8	90.3	104.2	98.2	94.4	SD: 9.43
	0.25	92.8	97.2	90.0	90.0	84.4	
	0.50	95.4	90.4	100.0	95.6	88.4	UCL: 124.5
	1.0	85.8	94.6	88.2	86.3	97.5	UWL: 115.1
	2.0	108.9	106.3	101.7	94.6	97.2	LWL: 77.3
	5.0	110.3	113.0	103.4	117.8	104.0	LCL: 67.9
Azinphos	0.05	85.4	59.0	98.6	71.2	92.8	Mean: 93.2
Methyl	0.10	79.6	4.2	96.0	107.4	95.2	SD: 14.58
	0.25	83.2	86.8	84.0	84.8	89.6	
	0.50	82.6	80.0	99.4	83.4	91.6	UCL: 136.9
	1.0	77.1	90.2	83.7	113.1	90.0	UWL: 122.3
	2.0	108.3	113.5	101.1	96.6	92.2	LWL: 64.0
	5.0	124.9	113.6	112.5	118.8	101.2	LCL: 49.4

APPENDIX II (Continued)

Method Validation Data and Control Limit

Analyte	Spike ppb	Recovery (%) Set 1	Set 2	Set 3	Set 4	Set 5	%
Dichlorvos	0.05	72.6	95.6	95.2	72.6	82.6	Mean: 82.6
	0.10	92.3	91.5	91.1	82.3	81.1	SD: 7.80
	0.25	87.2	78.0	77.6	87.2	77.2	
	0.50	83.0	79.0	85.0	83.0	55.6	UCL: 106.0
	1.0	82.9	82.3	79.1	82.9	77.2	UWL: 98.2
	2.0	82.1	82.5	92.2	80.7	78.7	LWL: 67.0
	5.0	83.5	99.0	81.6	90.0	76.2	LCL: 59.2
Phorate	0.05	83.4	89.0	95.6	83.4	86.8	Mean: 87.9
	0.10	82.8	90.5	97.6	82.8	85.3	SD: 7.21
	0.25	90.4	86.0	83.2	90.4	80.8	
	0.50	85.2	83.4	94.2	852	75.6	UCL: 109.5
	1.0	80.7	79.5	87.5	80.7	78.7	UWL: 102.3
	2.0	92.1	86.1	100.3	91.3	84.1	LWL: 73.5
	5.0	100.6	106.2	90.9	102.5	84.0	LCL: 66.3
Fonofos	0.05	88.2	92.0	101.4	88.2	89.4	Mean: 90.3
	0.10	85.9	92.2	100.4	85.9	87.3	SD: 7.40
	0.25	91.6	86.8	86.0	91.6	82.8	
	0.50	86.0	83.4	97.2	86.0	79.2	UCL: 112.5
	1.0	81.6	78.2	91.1	81.6	81.6	UWL: 105.1
	2.0	94.7	88.9	105.1	95.1	88.1	LWL: 75.5
	5.0	97.9	107.3	95.4	104.7	88.1	LCL: 68.1
Dimethoate	0.05	96.2	96.6	88.4	96.2	84.6	Mean: 90.5
	0.10	82.7	95.4	95.8	82.7	86.5	SD: 8.67
	0.25	93.2	82.4	82.8	93.2	78.8	
	0.50	91.8	76.0	97.8	91.8	79.2	UCL: 116.6
	1.0	104.2	68.2	97.7	104.2	83.2	UWL: 107.9
	2.0	88.5	89.7	103.6	93.6	90.8	LWL: 73.2
	5.0	92.6	101.0	86.4	106.2	87.0	LCL: 64.5

APPENDIX II (Continued)

Method Validation Data and Control Limit

Analyte	Spike ppb	Recovery (%) Set 1	Set 2	Set 3	Set 4	Set 5	%
Parathion Methyl	0.05	93.2	99.0	97.2	93.2	91.4	Mean: 93.7
	0.10	86.1	98.6	101.4	86.1	88.1	SD: 8.55
	0.25	97.2	87.2	92.8	97.2	82.4	
	0.50	91.4	81.2	105.2	91.4	79.8	UCL: 119.3
	1.0	98.9	73.4	110.8	98.9	84.2	UWL: 110.8
	2.0	91.9	90.3	105.9	98.6	91.6	LWL: 76.6
	5.0	97.2	105.1	90.2	111.5	90.5	LCL: 68.0
DEF	0.05	96.6	97.2	102.4	96.6	92.6	Mean: 95.3
	0.10	91.6	98.3	106.7	91.6	90.3	SD: 10.2
	0.25	94.0	88.0	96.0	94.0	84.8	
	0.50	92.2	77.6	112.0	92.2	83.4	UCL: 126.0
	1.0	84.3	69.4	108.7	84.3	84.9	UWL: 115.8
	2.0	99.7	94.4	115.1	103.2	93.8	LWL: 74.9
	5.0	103.5	99.7	104.2	118.1	95.9	LCL: 64.7
Profenofos	0.05	96.8	105.2	104.0	97.8	85.4	Mean: 94.3
	0.10	88.0	100.4	104.3	88.0	87.0	SD: 10.06
	0.25	102.0	84.0	94.8	102.0	83.2	
	0.50	95.6	73.0	107.0	95.6	79.8	UCL: 124.5
	1.0	98.5	63.5	105.8	98.5	87.9	UWL: 114.5
	2.0	93.6	91.5	106.5	99.	91.6	LWL: 74.2
	5.0	96.8	96.4	93.5	112.3	92.1	LCL: 64.1

APPENDIX III

Retention Time for OP Pesticides:

RT(min.) / Op Pesticides	Rtx® -OPPesticides column		Rtx® -OPPesticides2 column	
	30m x 0.25mm x 0.4μm	30m x 0.32mm x 0.5μm	30m x 0.25mm x 0.25μm	30m x 0.25mm x 0.32μm
Ethoprophos	11.7	9.7	11.7	9.6
Diazinon	12.5	10.4	13.6	11.2
Disulfoton	13.1	10.9	13.9	11.5
Chlorpyrifos	15.2	12.8	16.5	13.8
Malathion	16.3	13.8	16.2	13.5
Methidation	18.2	15.5	18.7	15.8
Fenamiphos	18.9	16.3	18.9	16.1
Azinphos methyl	23.9	21.0	25.1	21.8
Dichlorvos	8.4	7.0	7.8	6.3
Phorate	11.8	9.8	12.5	10.2
Fonofos	13.0	10.8	13.8	11.3
Dimethoate	14.4	12.0	13.6	11.1
Parathion methyl	16.4	13.8	15.5	12.8
Tribufos (DEF)	17.5	15.0	19.1	16.1
Profenofos	18.3	15.7	19.3	16.3

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Revision Log:

Date	What was Revised? Why?

Surface water continuing quality control

Bifenthrin Analysis

Extraction Date	Sample Numbers	Percent Recovery	
		spike 0.10 ppb	spike 1.0 ppb
5/25/99	142,124,118,106,100,58	84.4	none
6/30/99	128,146,170,190,195,201, (236)	99.0	96.5
9/27/99	177,207,219,225,345, 387,465,513,525	71.3	91.6
10/26/99	QC missing for bifenthrin screen for this set		
12/14/99	352,766,772,778,790, 820,850,862,916,946	89.5	99.8
1/19/00	538,82,542,743	91.1	91.6
1/20/00	478,592,622,826,952, 964	88.3	94.3
1/26/00	843,609,681,615,627, 339,753,585,831,795	73.5	84.3
1/26/00	867,699,660,471,588, 957,840,837,711,657	79.9	84.6
1/26/00	645,663,153,693,69,723, 363,747,165,603	81.0	93.5
1/27/00	159,87,561,651,687,729, 903,927,933	72.2	85.0
2/25/00	568,640,802,892,928, 940,982,1036,1054,1059, (1084),(1085)	100	103.0
3/29/00	460,718,970,988, 994,1000,1048, (1089)	103	92.1
4/21/00	382,580,634,676,886,1011,1018,1071,1094, 1100, (1110)	102	115
5/26/00	707,1125,1137,1145,1151,1157,1169,1175, (1196), 1216,1222	114	114
6/15/00	976,1115,1206,1232,1238,1250,1268,1274,1292	91.5	107
7/14/00	1106,1210,1256,1262, 1282,(1297)	82.9	104
8/4/00	1330,1348,1372,1377,1384,1390,1408,1414, 1420,(1426)	66.3	73.4
9/8/00	1163, 1306,1402,1450,1456, 1468,1476,1486, 1492,1498	103	110
10/20/00	1576,1570,1515,1564,1558,1552,1546,1342, 784,1354, (1430),1509	82.6	89.8
10/29/00	1533, 1538,1581,1584, 1593,1599,1605,1611, 1635,1638,1641,1647	89.1	96.6
11/17/00	1672,1527,1679,1666,1750,1714,1738,1732, 1744, 1720,1726	71.4	88.7
12/7/00	1708,1828,1792,1798, 1804,1696	98.0	100
12/7/00	1762,1768,1786,1822, 1702	100	99.2
1/19/01	(1440),1654,1810,1816,1840,1852	113	120
1/19/01	1660,1863,1869, 1888,1894,	103	104
2/1/01	1692, 1698	118	110
3/1/01	1876,1882,1930,1942,1946, (1960)	96.0	98.2
3/23/01	1918, 1924, 1983, 1988	107	100
4/27/01	(1846),1936,1995,2014,2020,2026	103	113
5/25/01	2032,2038,2044, 2056,2062,2068	93.0	93.9
6/14/01	2074,2080,2086,2092, 2104,2134	99.0	92.0

Extraction Date	Sample Numbers	Percent Recovery	
		spike 0.10 ppb	spike 1.0 ppb
7/27/01	2110, 2116,2146,1452,2260	107	110
8/3/01	2122,2128,2158,2164, 2187, 2189, (2206),2253	99.0	105
8/24/01	2220,2212,2218,2223,2230, 2236,2242	97.0	102
9/28/01	2314,2320,2326,2332,2350,2355, 2362	95.0	118
10/19/01	2255,2272,2278,2338,2344,2368, 2374,(2384)	103	105
11/29/01	2380,2440,2446,2452,2458,2512, 2518,	98.0	98.7
12/19/01	2398, 2404, 2410, 2428, 2434, 2491	96.0	95.8
1/9/02	2416,2422,2464,2469,2488, 2494, (2524)	87.0	97.0
2/15/02	2476,2481,2500,2506,2560, 2566,2572	102	104
2/15/02	2562	93.0	93.4
3/13/02	2548,2554,2643,2680, 2686	91.0	95.1
4/19/02	2649,2656,2662,2668,2674, 2961,2697,(2701)	99.0	88.1
5/30/02	2284,2290,2296,2301,2308, 2578,2584	88.0	110
6/14/02	2710,2716,2722,2728,2734, 2747,2752	99.0	99.7
8/16/02	(2705),2740,2758,2764,2770, 2776,2794,2800	78.0	84.2
Average Recovery		93.7	98.8
Standard Deviation		11.8	9.9
CV		12.6	10.0
Upper Control Limit		127	(same)127
Upper Warning Limit		117	117
Lower Warning Limit		74.9	74.9
Lower Control Limit		64.4	64.4

Highlighted cells are percent recoveries exceeding control limits
Method was not developed until May 1999
Sample numbers in parentheses are blind spikes

Fenoxycarb, Hydramethylnon and Pyriproxyfen Screen

Extraction Date	Sample Numbers	Percent Recovery - 1.0 ppb spike level		
		Fenoxycarb	Pyriproxyfen	Hydramethylnon
5/24/99-Spike 1		122	124	75.8
5/24/99-Spike 2*	101,59,107,119,125,143	100	107	74.6
6/30/99	131,149,173,191,197, 202	94.7	99.8	90.9
9/27/99	178,208,220,226,346, 388,466,514,526	94.0	97.8	76.3
10/26/99	QC missing for FHP screen for this set			
12/13/99	353,767,773,779,791,821,851,863,917, 949	86.3	87.3	53.4
1/19/00	429,593,623,827,953, 965	108	106	74.3
1/19/00	83,539,543, 744	106	100	75.9
2/4/00	154,166,364,604,610,646, 664,682,724, 845	94.1	93.1	79.5
2/4/00	616,628,340,754,586,832,796,868,658, 712	96.3	93.0	76.9
2/4/00	838,875,958,756,472,700,702,748,694,70	100	97.1	95.0
2/4/00	160,94,562,652,688,730,904 922, 934	100	98.1	75.1
2/25/00	569,641,803,893,926,941,83,1034,1055, 1061,(1077), (1078),(1079),(1080)	96.8	94.8	80.9
3/29/00	461,719,971,989,995, 1001,1049, (1090)	104	109	66.6
4/21/00	383,581,635,677,887,1012,1019,1070, 1095,1099, (1109)	110	109	94.8
5/25/00	708,1126,1138,1146,1152,1158,1170, 1176,(1197), 1217,1223	99.2	104	91.6
6/15/00	977,1116,1225,1233,1251,1269,1275, 1293	95.1	88.6	87.3
7/14/00	809, 1107,1211, 1257,1263,(1298)	96.6	92.1	72.3
8/4/00	1331,1349,1373,1378,1385,1391,1410, 1415,1421,(1427)	99.4	102	79.5
9/8/00-Spike 1	(1301),1307,1403,1451,1457,1469,1481,	94.1	109	112
9/8/00-Spike 2*	1487,1493, 1499	80.8	92.5	93.5
10/19/00	1577,1571,1516,1565,1559,1553,1547, 1343, 785,1355,1436,1510	98.3	99.2	84.2
10/29/00	1594,1534,1539,1600,1606,1608,1582, 1612,1636,1642,1648,1650	98.3	97.9	80.3
11/17/00-Spike 1	1528,1667,1673,1680,1715,1721,1728,	103	97.1	87
11/17/00-Spike 2*	1733,1739, 1745,1751,	102	96.3	90.6
12/7/00	1697,1703,1709, 1763, 1769	99.4	95.4	97.9
12/7/00	1787,1793,1799, 1805,1823,1829	98.4	93.1	86.5
1/19/01	1655,1661,1811,1817, 1841,1853	104	101	92.7
1/19/01	1864,1870,1889,1895,(1848),(1913)	97.2	98.7	92.3
6/14/01	2075,2081,2087,2093,2105, 2135	85.6	95.1	70.9
7/26/01	2111,2117,2147,2153, 2161	88.0	96.3	85.3
8/2/01	2123,(2207)	102	102	106

Extraction Date	Sample Numbers	Percent Recovery - 1.0 ppb spike level		
		Fenoxycarb	Pyriproxyfen	Hydramethylnon
8/23/01	2201,2213,2219,2224, 2231,2237, 2243	89.6	92.4	75.4
9/27/01	2315,2321,2327,2333,2351, 2356,2363	106	88.1	90.4
10/17/01	2256, 2275, 2279, 2339, 2345, 2369, 2375, 2387	93.7	96.0	71.8
11/29/01	2381,2441,2447,2453, 2459,2513,2519	103	107	94.6
12/19/01	2392,2399,2405,2411, 2429,2435	87.2	90.6	82.0
1/9/02	2417,2423,2465,2470, 2489,2495,2525,	88.1	76.2	83.8
2/22/02	2482,2501,2507,2561, 2567,2573,2477	83.0	92.5	76.3
3/18/02	2549,2555,2644,2681, 2687	99.1	108	62.3
4/19/02	2650,2657,2663,2669,2675,2692,2698, (2702)	96.8	105	81.9
5/30/02	2285,2291,2297,2302, 2309,2579,2585	111	109	109
5/30/02	2711,2717,2723,2729,2735,2748,2753	122	87.0	63.0
8/16/02	(2706),2741,2759,2765,2771,2777,2795, 2801, (2804)	104	96.3	89.3
Average Recovery		98.2	98.1	83.1
Standard Deviation		8.62	7.69	11.7
CV		8.77	7.83	14.1
Upper Control Limit		113	109	124
Upper Warning Limit		108	105	111
Lower Warning Limit		87.5	90.6	58.8
Lower Control Limit		82.4	87.0	45.7

*Spike 2 spiked at 0.4 ppb for the three analytes.
Highlighted cells are percent recoveries exceeding control limits
Method was not developed until May 1999
Sample numbers in parentheses are blind spikes

Organophosphate Screen from 3/29/99 to 8/7/00

Extraction Date	Sample Numbers	Percent Recovery						
		Chlorpyrifos	Dimethoate	Fonofos	Malathion	Methidathion	Methyl Parathion	Phosmet
5/24/99	55,97,103,115,121,139	95.0	94.0	95.0	98.0	97.0	96.0	91.4
6/30/99	127,145,169,184,187, 193, 235	88.8	92.0	82.0	91.0	93.0	89.0	89.6
9/28/99	175,205,217,223,343, 385,463,511,523	87.5	90.0	86.0	92.0	90.0	94.0	91.2
10/29/99	61,355,481,493,505, 530,547,554,571,595	104	101	103	104	103	101	98.6
12/14/99	349,763,769, 775	88.8	105	86.0	97.0	103	100	91.6
12/15/99	787,817,848,859,913, 943	88.8	104	95.0	95.0	102	99.0	103
1/21/00	79,475,489,535,(555), 589,619,740,823,949, 961	91.3	100	87.0	107	104	109	94.2
1/27/00	68,158,504,626,644, 680,709,835,995,(1075)	91.3	105	89.0	101	105	95.0	116
1/28/00	164,362,602,608,662, 692,722,746,842,865	92.5	101	90.0	98.0	107	101	99.2
1/28/00	86,152,583,614,650,72 8, 829 901,919,931	88.8	93.0	85.0	96.0	98.0	96.0	91.0
1/28/00	337,342,469,474,560, 655,686,697,751,793	98.8	105	96.6	105	108	104	102
2/28/00	565,637,799,889,925, 937,979,1033,1051, 1057,1082	92.5	102	90.0	104	112	99.0	106
3/31/00	457,715,967,985,991,9 97,1045, (1086)	98.8	94.0	92.0	113	97.0	111	96.6
4/25/00	379,577,631,673,883, 1008,1015,1074,1091, 1097,(1111)	92.5	101	87.0	101	101	96	101
5/30/00	705,1122,1134,1142,11 48,1154,1166,1172, 1213,1219	97.5	78.0	95.0	106	113	105	114
6/16/00	973,1112,1203,1229, 1235,1247,1265,1271, 1289	88.8	85.0	87.0	91.0	89.0	88.0	88.2
7/17/00	1103, 1190,1207,1221, 1253,1259,1279,(1295)	82.5	80.0	81.0	83.0	81.0	81.0	82.0
8/7/00	(1299),1327,1345,1369, 1375	105	105	103	110	113	108	105
8/7/00	1381, 387,1405,1411, 1417,1423	88.8	94.0	87.0	93.0	97.0	95.0	96.0
9/11/00	1303,1357,1359,(1435), 1447,1453,1465,1477, 1483,1489,1495	95.0	111	*NA*	102	107	*NA*	*NA*

Extraction Date	Sample Numbers	Percent Recovery						
		Chlorpyrifos	Dimethoate	Fonofos	Malathion	Methidathion	Methyl Parathion	Phosmet
10/20/00	781,1339,1351,(1424), 1507,1512,1543, 1549, 1555,1561,1567, 1573,	105	108	*NA*	111	113	*NA*	*NA*
10/30/00	1531,1536,1541,1579, 1591,1597,1602,1603, 1609,1633,1639, 1645	109	117	*NA*	113	117	*NA*	*NA*
11/20/00	1525,1663,1676,1711, 1717,1723,1729,1735, 1741,1747,	91.0	109	*NA*	102	112	*NA*	*NA*
12/8/00	1693,1699,1705,1759, 1765, 1783	83.0	113	*NA*	99.0	109	*NA*	*NA*
12/8/00	1789,1795,1802, 1819,1825	90.0	110	*NA*	99.0	109	*NA*	*NA*
1/22/01	(1437),1651,1657,1807, 1813,1837,1849,	90.1	112	*NA*	100	114	*NA*	*NA*
1/22/01	1861,1866,1885,1891, (1909)	89.7	108	*NA*	101	107	*NA*	*NA*
3/3/01	1873,1879,1927,1939, 1946,1957	86.0	84.3	*NA*	88.6	90.0	*NA*	*NA*
3/23/01	1915,1922,1979,1986	104	118	*NA*	110	115	*NA*	*NA*
4/27/01	(1843),1933,1992, (2010) 2011,2015,2024	93.9	110	*NA*	101	109	*NA*	*NA*
5/18/01	(1955),2030,2035,2041, 2053, 2059,2065	93.5	96.5	*NA*	106	119	*NA*	*NA*
6/14/01	2071,2077,2084,2089, 2101,2131	86.4	105	*NA*	91.8	104	*NA*	*NA*
7/30/01	2107,2113,2143,2149, 2258	90.4	97.0	*NA*	92.0	97.6	*NA*	*NA*
8/3/01	2119,2125,2130,2155, 2161,	83.4	79.9	*NA*	84.4	91.0	*NA*	*NA*
8/3/01	2184,2203, 2250	83.6	90.4	*NA*	90.4	91.0	*NA*	*NA*
8/24/01	2197,2209,2215,2221, 2227,2233,2239	86.9	119	*NA*	100	112	*NA*	*NA*
10/1/01	2311,2317,2323,2329, 2347,2353,2359	91.8	86.4	*NA*	91.8	93.4	*NA*	*NA*
10/18/01	2142,269,2273, 2335, 2341,365,2371, 2383	89.1	117	*NA*	98.8	110	*NA*	*NA*
Average Recovery		92.2	100	89.3	98.8	104	97.4	96.8
Standard Deviation		6.35	10.9	7.10	7.36	8.91	7.33	9.16
CV		6.89	10.7	7.95	7.44	8.60	7.53	9.46
Upper Control Limit		112	120	111	113	120	118	120
Upper Warning Limit		106	113	103	107	113	111	113
Lower Warning Limit		81.8	86.0	73.6	82.3	83.8	82.7	84.5
Lower Control Limit		75.1	79.0	66.3	76.1	76.6	75.7	77.4

NA= not analyzed
Continuing QC samples were spiked at 2x the reporting limit,; 0.08 ppb for chlorpyrifos, 0.10 for all other analytes
Highlighted cells are percent recoveries exceeding control limits
Sample numbers in parentheses are blind spikes

Organophosphate Screen from 11/30/01 to 8/19/02

Extraction Date	Sample Numbers	Percent Recovery			
		Dimethoate	Malathion	Chlorpyrifos	Methidathion
11/30/01	2377,2437,2443,2449,2455, 2510,2515	105	105	124	109
12/20/01	2389,2395,2401,2407,2425,2431	98.5	98.7	87.4	100
1/10/02	2413,2419,2461,2467,2485, 2491,2521,2528,	93.8	94.9	99.9	99
2/15/02	2473,2479,2497,2503,(2536), (2544),2557,2563, 2567	105	107	98.1	111
3/15/02	2545,2551,2641,2677, 2683	92.3	97.1	95.2	92.6
4/19/02	2646,2653,2659,2665,2671, 2689,2694	102	100	92.9	97.3
6/4/02	2281,2287,2293,2299, 2305, 2575, 2581	105	109	104	102
6/17/02	2707,2713,2719,2725, 2731, 2744, 2750	85.7	91.3	88.5	90.6
8/19/02	(2703),2737,2755,2761,2768, 2773,2791, 2797,(2803)	103	110	108	112
Average Recovery		98.8	102	97.9	101
Standard Deviation		7.97	7.39	7.28	9.04
CV		8.07	7.21	7.44	8.96
Upper Control Limit		117	126	121	128
Upper Warning Limit		108	116	112	117
Lower Warning Limit		73.2	75.7	76.9	74.6
Lower Control Limit		64.5	65.7	68.0	63.9

Continuing QC samples were spiked at 2x the reporting limit
Highlighted cells are percent recoveries exceeding control limits
Sample numbers in parentheses are blind spikes

Diazinon screen from 3/29/99 to 8/7/00

Extraction Date	Sample Numbers	Percent Recovery Diazinon Spike 0.08 ppb
5/24/99	57,99,105,117,123,141	67.5*
6/9/99	102,60,108,120,126,144	97.5
6/29/99	129,147,171,188,194,199, (237)	90.0
9/28/99	176,206,218,224,344,386 464,512,524	97.5
10/29/99	356,60,482,494,506,531, 548,(557),572,596	78.8
12/14/99	350,764, 770	98.8
12/15/99	776,778,818,849,860,914, 944	97.5
12/16/99	792	85.0
1/20/00	475,80,490,536,590,741,824,950,962	86.6
1/21/00	620,(556)	91.3
1/27/00	151,61,163,361,470,502, 613,656,691,745	89.0
1/28/00	338,85,559,685,727,841, 902,932,956,(1076)	101
1/28/00	601,607,643,649,661,679, 721,794,866,920	111
1/28/00	157,503,584,625,698,710, 714,752,830,836	83.8
2/25/00	566,638,800,890,929,938,980,1037,1052, 1058, (1081),(1083)	82.5
3/30/00	458,716,968,992,986,998, 1046, 1087	91.3
4/24/00	380,578,632,674,884, 1016,1073,1092,1098	85.0
5/30/00	706,1123,1135,1143,1149,1155,1167,1173, (1198),1214,1220	106
6/15/00	974, 1113,1204,1230,1236, 1248,1266,1272, 1290	98.0
7/17/00	1104,1191,1208,1224,1254,1260,1280,(1296)	103
8/7/00	1328,1346,1370, 1376,1382,1388,1406, 1412,1418	88.8
9/11/00	1304,1400,(1429),1448, 1454,1466,1478, 1484,1490,1496	96.8
10/23/00	1574,1568,1513,1562,1556,1550,1544,1340, 1476,1352, 1508	101
10/30/00**	1634, 1592,1532,1537, 1542,1580,1598,1604, 1610,1614,1640,1646	86.0
11/21/00	1526,1664,1670, 1677,1712,1718,1724, 1739,1736,1742,1748,	92.6
1/22/01	(1438),1652,1658,1808,1814,1832,1838, 1850,1862	83.8
1/22/01	1867,1886,1892,1898	91.2
3/2/01	1874,1880,1928,1940, 1947,(1958)	88.6
3/23/01	1916,1923,1975,1987	74.9
4/27/01	(1844),1934,1993,2012, 2016,2025	90.0
5/29/01	(1956),2031,2036,2042,2054,2060,2066	82.5
6/15/01	2072,2078,2085,2090, 2102,2132	88.8
7/27/01	2108,2114,2144, 2150,2259	105

Extraction Date	Sample Numbers	Percent Recovery Diazinon Spike 0.08 ppb
8/6/01	2120,2126,2156, 2162,2166	84.0
8/6/01	2185,2204,2251	87.4
8/27/01	2198,2210,2216,2222, 2228,2234,2240	92.1
9/28/01	2312, 2318,2324,2330, 2348, 2354,2360	97.1
10/18/01	2178,2270,2274,2336, 2342,2366,2372,2386	118
Average Recovery		91.2
Standard Deviation		17.4
CV		19.1
Upper Control Limit		109
Upper Warning Limit		103
Lower Warning Limit		77.6
Lower Control Limit		71.4

* Diazinon spike was low, backups analyzed 6/9/99
**spiked at 0.8ppb instead of 0.08 ppb
Highlighted cells are percent recoveries exceeding control limits
Sample numbers in parentheses are blind spikes

Diazinon Screen from 11/30/01 to 8/19/02

Extraction Date	Sample Numbers	Percent Recovery Diazinon Spike 0.08 ppb
11/30/01	2378,2438,2444,2450, 2456,2511,2516	79.1
12/20/01	2390,2396,2402,2408, 2426, 2432	95.1
1/14/02	2414, 2420, 2462, 2468, 2486, 2492, 2522,	79.3
2/15/02	2474,2480,2498,2504,(2537),2558,2564, 2570	104
3/15/02	2546,2552,2642,2678, 2684	91.5
4/19/02	2647,2654,2660,2666, 2672,2690,2695	108
5/31/02	2282,2288,2294,2300, 2306,2576,2582	83.9
6/17/02	2708,2714,2720,2726, 2732,2745,2751	97.9
8/19/02	2738,2756,2762, 2774,2792,2798,2769,2704	105
Average Recovery		93.7
Standard Deviation		11.0
CV		11.7
Upper Control Limit		147
Upper Warning Limit		130
Lower Warning Limit		62.9
Lower Control Limit		46.1

Highlighted cells are percent recoveries exceeding control limits
Sample numbers in parentheses are blind spikes

Blind Spike Recoveries for RIFA surface water

Extraction Date	Sample Number	Screen	Pesticide	Spike Level	Recovery	Percent Recovery	Exceed CL*
6/29/99	237	DI	Diazinon	0.2	0.177	88.5	
6/30/99	235	OP	Chlorpyrifos	0.1	0.100	100	
6/30/99	236	BI	Bifenthrin	0.2	0.151	75.5	
10/29/00	553	FHP	Pyriproxyfen	0.3	0.262	87.3	
10/29/99	558	BI	Bifenthrin	0.2	0.161	80.5	
10/29/99	557	DI	Diazinon	0.1	0.085	85.0	
10/29/99	554	OP	Dimethoate	0.1	0.093	93.0	
1/21/00	556	DI	Diazinon	0.2	0.194	97.0	
1/21/00	555	OP	Methyl Parathion	0.2	0.196	98.0	
			Chlorpyrifos	0.2	0.200	100	
1/27/00	1075	OP	Dimethoate	0.3	0.324	108	
1/28/00	1076	DI	Diazinon	0.3	0.267	89.0	
2/25/00	1079[a]	FHP	Pyriproxyfen	0.3	0.285	95.0	
2/25/00	1077[a]	FHP	Pyriproxyfen	0.3	0.320	107	UWL
2/25/00	1078[b]	FHP	Fenoxycarb	0.3	0.267	89.0	
			Hydramethylnon	0.4	0.224	56.0	LWL
2/25/00	1080[b]	FHP	Fenoxycarb	0.3	0.266	88.7	
			Hydramethylnon	0.4	0.202	50.5	LWL
2/25/00	1083[c]	DI	Diazinon	0.2	0.184	92.0	
2/25/00	1081[c]	DI	Diazinon	0.2	0.179	89.5	
2/25/00	1084[d]	BI	Bifenthrin	0.2	0.133	66.5	LWL
2/25/00	1085[d]	BI	Bifenthrin	0.2	0.139	69.5	LWL
2/28/00	1082	OP	Chlorpyrifos	0.3	0.232	77.3	LWL
3/29/00	1090	FHP	Fenoxycarb	0.3	0.243	81.0	LCL
3/29/00	1089	BI	Bifenthrin	0.4	0.361	90.3	
3/30/00	1087	DI	Diazinon	0.2	0.159	79.5	
3/31/00	1086	OP	Chlorpyrifos	0.3	0.291	97.0	
			Methyl Parathion	0.4	0.434	109	
4/21/00	1110	BI	Bifenthrin	0.2	0.161	80.5	
4/21/00	1109	FHP	Hydramethylnon	0.4	0.398	99.5	
4/25/00	1111	OP	Dimethoate	0.2	0.201	101	
			Phosmet	0.3	0.269	89.7	
5/25/00	1197	FHP	Hydramethylnon	0.3	0.219	73.0	
5/26/00	1196	BI	Bifenthrin	0.3	0.269	89.7	
5/30/00	1198	DI	Diazinon	0.2	0.147	73.5	LWL
7/14/00	1297	BI	Bifenthrin	0.2	0.214	107	
7/17/00	1296	DI	Diazinon	0.2	0.181	90.5	
7/17/00	1295	OP	Chlorpyrifos	0.3	0.281	93.7	

Extraction Date	Sample Number	Screen	Pesticide	Spike Level	Recovery	Percent Recovery	Exceed CL*
8/4/00	1426	BI	Bifenthrin	0.25	0.172	68.8	LWL
8/7/00	1299	OP	Dimethoate	0.25	0.251	100	
8/7/00	1423	OP	Chlorpyrifos	0.25	0.210	84.0	
9/8/00	1301	FHP	Hydramethylnon	0.5	0.248	49.6	LCL
			Pyriproxyfen	0.3	0.293	97.7	
9/11/00	1435	OP	Dimethoate	0.15	0.164	109.3	
9/11/00	1429	DI	Diazinon	0.2	0.175	87.5	
10/19/00	1436	FHP	Fenoxycarb	0.4	0.364	91.0	
			Hydramethylnon	2.0	1.39	69.5	
10/20/00	1424	OP	Chlorpyrifos	0.3	0.321	107	UWL
			Malathion	0.2	0.211	106	
10/20/00	1430	BI	Bifenthrin	0.3	0.236	78.7	
1/19/01	1848	FHP	Hydramethylnon	1.0	0.742	74.2	
1/19/01	1913	FHP	Fenoxycarb	0.3	0.304	101	
1/19/01	1440	BI	Bifenthrin	0.5	0.513	103	
1/22/01	1437	OP	Chlorpyrifos	0.3	0.335	112	UWL
1/22/01	1909	OP	Chlorpyrifos	0.25	0.225	90.0	
1/22/01	1438	DI	Diazinon	0.3	0.249	83.0	
3/1/01	1957	OP	Chlorpyrifos	0.35	0.303	86.6	
3/1/01	1960	BI	Bifenthrin	0.4	0.325	81.3	
3/1/01	1961	FHP	Fenoxycarb	0.35	0.307	87.7	
3/2/01	1958	DI	Diazinon	0.4	0.331	82.8	
4/26/01	1847	FHP	Pyriproxyfen	0.3	0.281	93.7	
4/27/01	1843	OP	Chlorpyrifos	0.3	0.281	93.7	
4/27/01	1844	DI	Diazinon	0.25	0.222	88.8	
4/27/01	1846	BI	Bifenthrin	0.35	0.269	76.9	
4/27/01	2010	OP	Malathion	0.2	0.211	106	
5/18/01	1955	OP	Chlorpyrifos	0.5	0.417	83.4	
			Dimethoate	0.1	0.110	110	
			Malathion	0.2	0.183	91.5	
5/21/01	1956	DI	Diazinon	0.2	0.162	81.0	
8/2/01	2207	FHP	Fenoxycarb	0.2	0.192	96.0	
			Pyriproxyfen	0.2	0.194	97.0	
8/3/01	2206	BI	Bifenthrin	0.25	0.182	72.8	
8/6/01	2204	DI	Diazinon	0.25	0.188	75.2	LWL
8/3/01	2203	OP	Chlorpyrifos	0.2	0.176	88.0	
10/17/01	2387	FHP	Fenoxycarb	0.15	0.143	95.3	
			Hydramethylnon	0.45	0.301	66.9	LWL
10/18/01	2384	BI	Bifenthrin	0.35	0.307	87.7	
10/18/01	2386	DI	Diazinon	0.15	0.161	107	UWL

Extraction Date	Sample Number	Screen	Pesticide	Spike Level	Recovery	Percent Recovery	Exceed CL*
10/18/01	2383	OP	Chlorpyrifos	0.25	0.218	87.2	
			Dimethoate	0.35	0.363	104	
1/9/02	2524	BI	Bifenthrin	0.25	0.221	88.4	
1/9/02	2525	FHP	Pyriproxyfen	0.2	0.110	55.0	LCL
1/10/02	2528	OP	Dimethoate	0.2	0.182	91.0	
			Malathion	0.3	0.281	93.7	
1/10/02	2521	OP	Chlorpyrifos	0.25	0.202	80.8	
1/14/02	2522	DI	Diazinon	0.25	0.206	82.4	
2/15/02	2536	OP	Chlorpyrifos	0.2	0.172	86.0	
2/15/02	2544	OP	Dimethoate	0.25	0.163	65.2	LCL
2/15/02	2537	DI	Diazinon	0.25	0.266	106	
4/19/02	2702	FHP	Pyriproxyfen	0.5	0.485	97.0	
4/19/02	2701	BI	Bifenthrin	0.25	0.158	63.2	LCL
8/16/02	2705	BI	Bifenthrin	0.45	0.397	88.2	
8/16/02	2804	FHP	Fenoxycarb	0.3	0.332	111	UWL
8/16/02	2706	FHP	Pyriproxyfen	0.5	0.484	96.8	
8/19/02	2704	DI	Diazinon	0.35	0.34	97.1	
8/19/02	2703	OP	Methidathion	0.2	0.176	88.0	
8/19/02	2803	OP	Dimethoate	0.25	0.189	75.6	
			Malathion	0.4	0.314	78.5	

* CL= control limits

a duplicate spikes-relative percent difference 11.9%

b duplicate spikes-relative percent difference 0.337% for fenoxycarb and 10.3% for hydramethylnon

c duplicate spikes-relative percent difference 2.75%

d duplicate spikes-relative percent difference 4.41%

Two additional spikes were sent in for hydramethylnon on 7/14/00 and 8/4/00. Results are not on table because the spike level requested was too low and thus a recovery within control limits would be below the RL, and the other because the spike may have dissipated in 4 days between spiking to extraction.

Well sampling continuing quality control

Bifenthrin Analysis

Extraction Date	Sample Numbers	Percent Recovery Bifenthrin spike 0.10 ppb	Bifenthrin spike 1.0 ppb
11/15/2000	10,16,22,40,46,64	69.9	100
3/1/2001	4,28,58	104	109
7/27/2001	52,76,80	104	105
6/14/2002	88,94,100,106,112,118	98.0	101
Average Recovery		94.0	104
Standard Deviation		16.3	4.10
Coefficients of Variability		17.3	4.00
Upper Control Limit		94.0	94.0
Upper Warning Limit		89.0	89.0
Lower Warning Limit		78.2	78.2
Lower Control Limit		72.9	72.9

*Highlighted cells are percent recoveries exceeding control limits

Fenoxycarb, Hydramethylnon and Pyriproxyfen Screen

Extraction Date	Sample Numbers	Percent Recovery - 1.0 ppb spike Fenoxycarb	Hydramethylnon	Pyriproxyfen
11/15/2000	11,17,23,41,47,65	105	92.8	98.8
3/1/2001	5,29,59	91.8	91.2	101
7/26/2001	53,77,81	83.2	71.2	93.3
6/12/2002	89,95,101,107,113,119	112.0	58.3	91.5
Average Recovery		98.0	78.4	96.2
Standard Deviation		12.9	16.6	4.5
Coefficients of Variability		13.2	21.2	4.7
Upper Control Limit		121	109.0	120
Upper Warning Limit		107	96.0	108
Lower Warning Limit		78.5	70.5	85.5
Lower Control Limit		64.4	57.7	74.1

Organophosphate Screen

Extraction Date	Sample Numbers	Percent Recovery- Dimethoate- 0.1 ppb spike	Malathion- 0.1 ppb spike	Chlorpyrifos- 0.08 ppb spike	Methidathion- 0.1 ppb spike
11/20/2000	7,13,19,37,43,63	108	105	96.8	109
3/2/2001	1,25,55	105	99.4	92.2	109
7/30/2001	49,73,79	107	111	104	112
6/17/2002	85,91,97,103,109,115	95.0	95.6	95.9	94.3
Average Recovery		104	103	97.2	106
Standard Deviation		6.0	6.8	4.9	8.1
Coefficients of Variability		5.8	6.6	5.0	7.6
Upper Control Limit		120	113	112	120
Upper Warning Limit		113	107	106	113
Lower Warning Limit		86.0	82.3	81.8	83.8
Lower Control Limit		79.0	76.1	75.1	76.6

Diazinon Analysis

Extraction Date	Sample Numbers	Percent Recovery- 0.08 ppb spike Diazinon
11/20/2000	8,14,20,38,44,62	103
3/2/2001	2,26,56	87.9
7/27/2001	50,74	92.0
6/14/2002	86,92,98,104,110,116	89.1
Average Recovery		93.0
Standard Deviation		6.9
Coefficients of Variability		7.4
Upper Control Limit		126
Upper Warning Limit		115
Lower Warning Limit		72
Lower Control Limit		76

Blind Spike Recoveries for RIFA Well sampling

Extraction Date	Sample Number	Screen	Pesticide	Spike Level	Recovery	Percent Recovery	Exceed CL*
7/26/2002	81	FHP	Hydramethylnon	3.0	2.18	72.7	No
			Pyriproxyfen	0.5	0.43	86.0	No
7/27/2002	80	Bifenthrin	Bifentrin	0.3	0.266	88.7	No
7/30/2002	79	OP	Chlorpyrifos	0.1	0.086	85.8	No
			Malathion	0.2	0.19	95.0	No

* CL= control limits

Storage Stability

Storage stability tests were conducted on all matrices to determine if there would be any dissipation of the analytes when samples were stored. All tests were conducted by CDFA Center for Analytical Chemistry under similar conditions as samples were kept in the field. Usually a QC blank and a QC spike sample were created and analyzed on the day the storage sample was removed and analyzed. All blanks were non detect and the QC spike sample results are shown on the storage stability tables (Tables 1 through 4). Stability testing was conducted on surface water, no testing was done for ground water.

Eight liters of water were spiked with 2.0 parts per billion each of fenoxycarb, hydramethylnon and pyriproxyfen and stored in a refrigerator at 4°C. A pair of water samples were removed from the refrigerator, extracted and analyzed on days 0, 3, 18 and 36. The results indicated that fenoxycarb is very stable under these storage conditions (slope of QC and sample recoveries very similar) (Table 1; Figure 1); pyriproxyfen is fairly stable, but should be extracted within 10 days or sooner (Table 2, Figure 2); and hydramethylnon sample recoveries past day three were much less than the QC samples (Table 3, Figure 3), which show that it is not as stable and should be extracted within 3-4 days.

Twenty-one liters of American River water were spiked with 0.25 ppb of bifenthrin as well as several other pyrethroid insecticides. 0.5g of sediment was added to each liter of matrix water to simulate runoff water. Various studies have shown that pyrethroid insecticides adhere to sediment. Three spiked water samples were removed on days 0, 3, 6, 9, 13, 30 and 37, and then analyzed. The bifenthrin results are shown in Table 4 and Figure 4. Results indicate that bifenthrin is fairly stable but should be extracted within 3-4 days.

Storage stability data for the old OP method (163) can be found in Ross et. al. (1996). When that storage stability study was conducted, it was determined that acidifying water with HCL to a pH between 3 and 3.5 stabilized most OP's except diazinon. OP samples were acidified for this study and diazinon was taken in a separate sample even when the newer OP method was developed (262). The OP and diazinon samples were very stable under these conditions.

Table 1.
Fenoxycarb

Day	Rep #1 Recovery	Rep #2 Recovery	Mean Recovery	QC Spike
0	90.5	85.8	88.2	99.7
3	96.1	99.0	97.6	90.3
18	98.8	95.9	97.4	97.9
36	100.0	99.6	100	101

Figure 1.

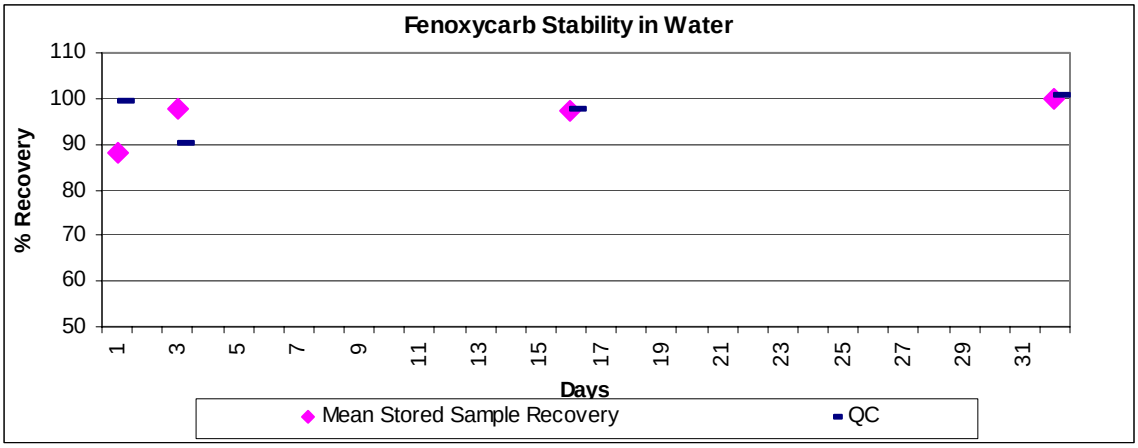


Table 2.

Pyriproxyfen

Day	Rep #1 Recovery	Rep #2 Recovery	Mean Recovery	QC Spike
0	95.2	89.6	92.4	102
3	98.4	94.6	96.5	92.9
18	84.0	81.6	82.8	99.0
36	80.9	79.9	80.4	103

Figure 2.

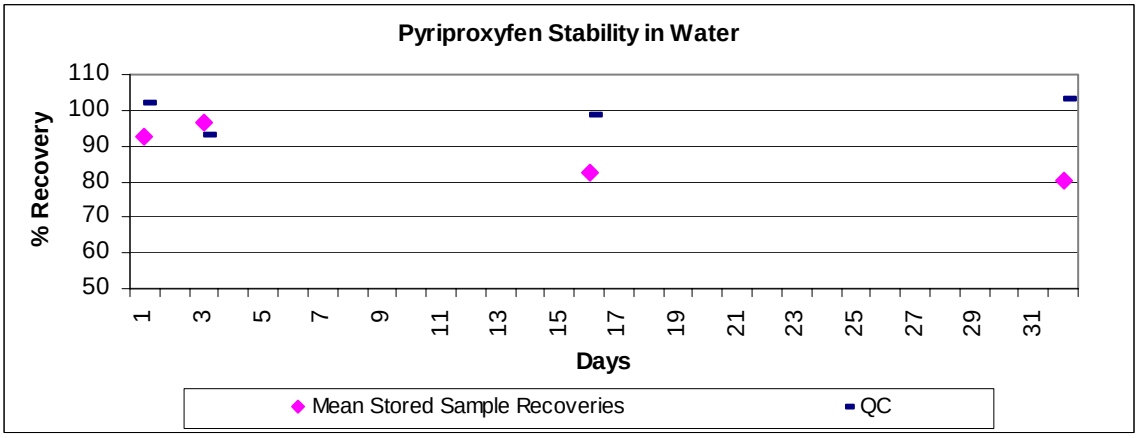


Table 3.

Hydramethylnon

Day	Rep #1 Recovery	Rep #2 Recovery	Mean Recovery	QC Spike
0	83.4	71.1	77.3	101
3	81.0	85.0	83.0	89.8
18	69.6	75.5	72.6	87.7
36	53.2	48.2	50.7	89.0

Figure 3.

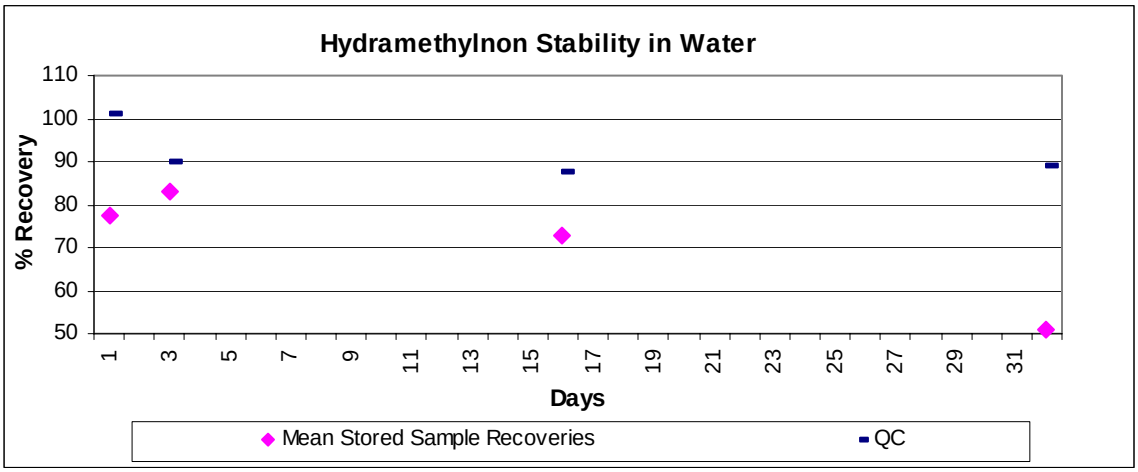
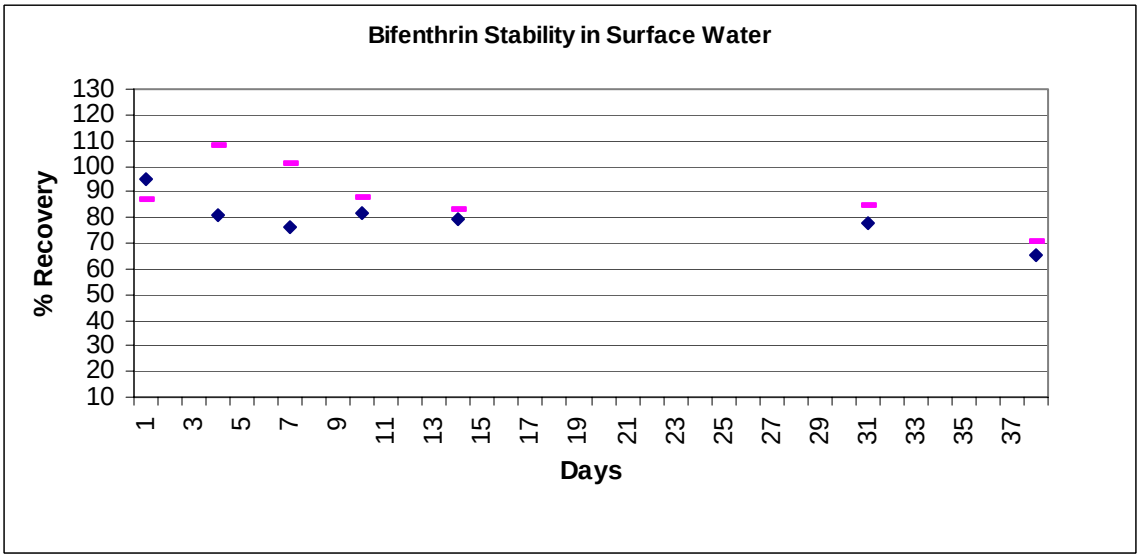


Table 4.

Bifenthrin

Day	Rep #1 Recovery	Rep #2 Recovery	Rep #3 Recovery	Mean Recovery	QC Spike
0	90.6	100	88	95.3	87.1
3	77.3	77.0	89.2	81.2	108
6	84.6	69.8	74.5	76.3	101
9	78.4	65.7	100	81.4	88.0
13	85.2	77.2	74.8	79.1	83.0
30	72.8	84.2	75.9	77.6	85.0
37	66.0	59.7	69.8	65.2	70.7

Figure 4.



Appendix B

Sampling Results

Monthly Sampling
Rain Event

Site A Bolsa Chica Channel

Site	Date	Bifenthrin	Fenoxycarb	Hydramethylnon	Pyriproxyfen	Chlorpyrifos	Diazinon	Dimethoate	Fonophos	Malathion	Methidathion	Methyl Parathion	Phosmet	Percent Mortality	Temp. °C	pH	EC (µS/cm)	DO (mg/L)	Ammonia mg/L NH3	Alkalinity mg/L CaCO3	Hardness mg/L CaCO3
BCC	5/21/1999	ND	ND	ND	ND	ND	0.07	ND	ND	ND	ND	ND	ND	0	17.0	7.4	2500	6.6	NT	442	555
BCC	6/25/1999	ND	ND	ND	ND	ND	0.11	ND	ND	ND	ND	ND	ND	0	19.0	7.3	2270	8.2	NT	378	510
BCC	9/23/1999	ND	ND	ND	ND	ND	0.22	ND	ND	ND	ND	ND	ND	15	26.8	NT	2060	19.5	<1	146	400
BCC	10/27/1999	ND	ND	ND	ND	ND	0.24	ND	ND	ND	ND	ND	ND	50*	17.6	7.7	2100	3.77	NT	338	392
BCC	12/9/1999	ND	ND	ND	ND	ND	0.21	ND	ND	ND	ND	ND	ND	75**	10.0	8.4	220	9.29	<1	383	472
BCC	1/18/2000	ND	ND	ND	ND	ND	0.63†	ND	ND	ND	ND	ND	ND	100*	14.2	8.2	2160	6.68	<1	146	132
BCC	2/23/2000[1]	ND	ND	ND	ND	ND	0.29	ND	ND	0.09	ND	ND	ND	100*	14.0	8.2	145	9.6	<1	38	40
BCC	3/27/2000	ND	ND	ND	ND	ND	0.08	ND	0.1	ND	ND	ND	ND	20	21.1	8.8	2519	13.03	<1	354	450
BCC	4/19/2000[2]	ND	ND	ND	ND	ND	0.38	ND	0.07	ND	ND	ND	ND	100*	21.2	8.1	1149	7.96	<1	196	254
BCC	5/24/2000	ND	ND	ND	ND	ND	0.19	ND	ND	ND	ND	ND	ND	15	19.3	8.2	1922	6.9	<1	308	364
BCC	6/13/2000	ND	ND	ND	ND	ND	0.08	ND	ND	ND	ND	ND	ND	0	32.2	9.0	2200	17.71	<1	188	254
BCC	8/1/2000	ND	ND	ND	ND	ND	0.11	ND	ND	ND	ND	ND	ND		27.8	8.7	2099	13.8			
BCC	9/6/2000	ND	ND	ND	ND	ND	0.10	ND		ND	ND				24.9	8.5	1905	12.02			
BCC	10/18/2000	ND	ND	ND	ND	ND	0.14	ND		ND	ND				21.4	8.2	2134	12.33			
BCC	11/15/2000	ND	ND	ND	ND	ND	0.51†	ND		ND	ND				15.7	8.4	2333	13.7			
BCC	12/5/2000	ND	ND	ND	ND	ND	0.14	ND		ND	ND				12.5	7.6	2289	5.8			
BCC	1/17/2001	ND	ND	ND	ND	ND	0.09	ND		ND	ND				14.2	7.4	2576	8.28			

* =survival significantly less than the control group (P< 0.05)
** =survival not significantly different from control due to replicate variability
† =greater than the LC50 for C. dubia

[1] = 0.07 inches of rain fell on 2/23/2000; 0.61 inches of rain fell on 2/22/2000
[2] = 1.13 inches of rain fell on 4/18/2000

Site B East Garden Grove

Site	Date	Bifenthrin	Fenoxycarb	Hydramethylnon	Pyriproxyfen	Chlorpyrifos	Diazinon	Dimethoate	Fonophos	Malathion	Methidathion	Methyl Parathion	Phosmet	Percent Mortality	Temp. °C	pH	EC (µS/cm)	DO (mg/L)	Ammonia mg/L NH3	Alkalinity mg/L CaCO3	Hardness mg/L CaCO3
EGG	6/25/1999	ND	ND	ND	ND	ND	0.11	ND	ND	ND	ND	ND	ND	0	20.0	7.2	1668	3.1	NT	240	438
EGG	9/23/1999	ND	ND	ND	ND	ND	0.11	ND	ND	ND	ND	ND	ND	0	24.0	NT	1420	16.65	<1	300	360
EGG	10/27/1999	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10	18.0	7.9	15	4.48	NT	316	404
EGG	12/9/1999	ND	ND	ND	ND	ND	0.12	ND	ND	ND	ND	ND	ND	40**	9.5	8.2	800	9.1	<1	420	520
EGG	1/18/2000	ND	ND	ND	ND	ND	0.13	ND	ND	ND	ND	ND	ND	5	14.3	8.1	1631	6.22	<1	390	440
EGG	2/23/2000[1]	ND	ND	ND	ND	0.41†	0.14	ND	ND	0.08	ND	ND	ND	30	14.3	8.0	92	9.2	<1	26	30
EGG	3/27/2000	ND	ND	ND	ND	ND	0.14	ND	ND	0.42	ND	ND	ND	0	20.1	9.1	1482	18.61	19.2	300	408
EGG	4/19/2000[2]	ND	ND	ND	ND	ND	0.10	ND	0.08	ND	ND	ND	ND	0	19.5	7.8	439	8.33	<1	98	124
EGG	5/24/2000	ND	ND	ND	ND	ND	0.12	ND	ND	ND	ND	ND	ND	20	20.0	7.9	1587	3.45	<1	310	396
EGG	6/13/2000	ND	ND	ND	ND	ND	0.07	ND	ND	ND	ND	ND	ND	0	31.3	8.6	1567	13.13	<1	232	292
EGG	8/1/2000	ND	ND	ND	ND	ND	0.26	ND	ND	ND	ND	ND	ND		26.7	8.7	1180	13.88			
EGG	9/6/2000	ND	ND	ND	ND	ND	0.12	ND		ND	ND				23.8	8.2	1393	10.12			
EGG	10/18/2000	ND	ND	ND	ND	ND	0.19	ND		ND	ND				21.2	8.5	907	10.28			
EGG	11/15/2000	ND	ND	ND	ND	ND	0.12	ND		ND	ND				13.5	8.3	1180	12.6			
EGG	12/5/2000	ND	ND	ND	ND	ND	0.10	ND		ND	ND				13.6	7.6	1516	6.21			
EGG	1/17/2001	ND	ND	ND	ND	ND	0.12	ND		ND	ND				12.3	7.3	664	9.13			

* =survival significantly less than the control group (P< 0.05)
** =survival not significantly different from control due to replicate variability
† =greater than the LC50 for C. dubia

[1] = 0.07 inches of rain fell on 2/23/2000; 0.61 inches of rain fell on 2/22/2000
[2] = 1.13 inches of rain fell on 4/18/2000

Site C Westcliff Park

Site	Date	Bifenthrin	Fenoxycarb	Hydramethylnon	Pyriproxyfen	Chlorpyrifos	Diazinon	Dimethoate	Fonophos	Malathion	Methidathion	Methyl Parathion	Phosmet	Percent Mortality	Temp. °C	pH	EC (µS/cm)	DO (mg/L)	Ammonia mg/L NH3	Alkalinity mg/L CaCO3	Hardness mg/L CaCO3
WCP	12/9/1999	ND	ND	ND	ND	0.13	2.25†	ND	ND	ND	0.05	ND	ND	100*	13.3	9.1	1088	NT	<1	230	340
WCP	1/18/2000	ND	ND	ND	ND	ND	0.45	ND	0.05	ND	ND	ND	ND	100*	23.3	9.6	1929	NT	<1	160	240
WCP	2/24/2000[1]	ND	ND	ND	ND	ND	0.17	ND	ND	0.15	ND	ND	ND	80*	14.2	9.1	1260	13.48	<1	100	320
WCP	4/19/2000[2]	ND	ND	ND	ND	ND	0.10	ND	ND	ND	ND	ND	ND	5	NT	10.2	NT	NT	<1	98	198
WCP	5/24/2000	ND	ND	ND	ND	ND	0.32	ND	0.22	ND	0.09	0.12	ND	100*	23.7	8.0	1051	8.01	<1	140	300
WCP	6/13/2000	ND	ND	ND	ND	ND	0.14	ND	ND	ND	ND	ND	ND	25*	29.9	10.1	496	NT	<1	222	280
WCP	7/12/2000	ND	ND	ND	ND	ND	0.27	ND	ND	0.12	ND	ND	ND		20.7	8.7	490	10.28			
WCP	8/1/2000	ND	ND	ND	ND	ND	0.11	ND	0.21	ND	ND	ND	ND		33.8	10.2	890	14.37			
WCP	9/6/2000	ND	ND	ND	ND	ND	0.22	ND		ND	ND				33.1	9.7	688	14.86			
WCP	10/18/2000	ND	ND	ND	ND	0.33†	0.23	ND		0.21	ND				21.0	9.1	950	13.25			
WCP	11/16/2000	ND	ND	ND	ND	0.05	ND	ND		0.21	ND				18.9	9.5	817	14.29			
WCP	12/5/2000	ND	ND	ND	ND	0.06	0.33	ND		0.11	ND				17.9	9.3	565	NT			
WCP	1/17/2001	0.05	ND	ND	ND	ND	0.97†	ND		0.19	ND				12.0	8.0	350	11.28			
WCP	4/25/2001	ND	ND	ND	ND	ND	0.07	ND		ND	ND				28.5	8.5	3340	NA			
WCP	5/16/2001	ND	ND	ND	ND	ND	0.13	ND		ND	0.06				21.1	8.1	NA	14.67			
WCP	6/12/2001	ND	ND	ND	ND	ND	15.5†	ND		5.55†	ND				21.2	9.0	1103	12.85			
WCP	7/24/2001	ND	ND	ND	ND	ND	0.94†	ND		ND	ND				32.7	9.1	964	15.15			
WCP	8/22/2001	ND	ND	ND	ND	ND	0.10	ND		ND	ND				21.3	8.7	938	14.33			
WCP	9/25/2001	ND	ND	ND	ND	ND	12.25†	ND		ND	ND				29.4	8.5	1328	13.13			
WCP	10/16/2001	ND	ND	ND	ND	ND	0.14	ND		ND	ND				26.5	8.9	938	14.61			
WCP	11/28/2001	ND	ND	ND	ND	ND	0.15	ND		0.38	ND				16.0	8.7	380	15.5			
WCP	12/18/2001	ND	ND	ND	ND	ND	0.15	0.28		0.07	ND				16.3	8.5	874	16.3			
WCP	1/8/2002	ND	ND	ND	ND	ND	2.85†	ND		ND	ND				19.3	9.9	330	17.62			
WCP	2/14/2002	0.08	ND	ND	ND	ND	0.69†	ND		ND	ND				21.5	9.8	1322	16.44			
WCP	3/12/2002	ND	ND	ND	ND	ND	0.08	ND		ND	ND				26.1	9.8	789	15.71			
WCP	4/18/2002	ND	ND	ND	ND	ND	0.16	ND		ND	ND				25.6	9.6	853	NT			
WCP	5/29/2002	ND	ND	ND	ND	ND	0.15	ND		ND	ND				29.2	9.9	617	NT			

WCP	6/12/2002	ND	ND	ND	ND	ND	0.34	ND	ND	ND	32.5	10.3	731	14.33
WCP	8/14/2002	ND	ND	ND	ND	ND	0.11	ND	ND	ND	22.5	9.1	997	15.36

* =survival significantly less than the control group (P< 0.05)
** =survival not significantly different from control due to replicate variability
† =greater than the LC50 for C. dubia

[1] = 0.30 inches of precipitation fell on 2/23/2000
[2] = 0.40 inches of precipitation fell on 4/18/2000

Site D Bonita Creek

Site	Date	Bifenthrin	Fenoxycarb	Hydramethylnon	Pyriproxyfen	Chlorpyrifos	Diazinon	Dimethoate	Fonophos	Malathion	Methidathion	Methyl Parathion	Phosmet	Percent Mortality	Temp. °C	pH	EC (µS/cm)	DO (mg/L)	Ammonia mg/L NH3	Alkalinity mg/L CaCO3	Hardness mg/L CaCO3
BC	9/23/1999	ND	ND	ND	ND	ND	0.24	ND	ND	0.06	ND	ND	ND	15	NT	NT	3150	NT	<1	250	1050
BC	10/27/1999	ND	ND	ND	ND	ND	0.13	ND	ND	ND	ND	ND	ND	60*	16.4	8.3	2990	NT	NT	322	746
BC	12/9/1999	ND	ND	ND	ND	ND	0.26	ND	ND	ND	ND	ND	ND	100*	9.2	8.4	3229	10.36	<1	450	890
BC	1/18/2000	ND	ND	ND	ND	ND	0.05	ND	ND	ND	ND	ND	ND	100*	13.9	8.2	1930	10.4	<1	240	430
BC	2/24/2000[1]	ND	ND	ND	ND	ND	0.07	ND	ND	ND	ND	ND	ND	15	10.1	7.8	1412	9.37	<1	148	360
BC	3/28/2000	ND	ND	ND	ND	ND	0.05	ND	ND	ND	ND	ND	ND	15	13.3	8.2	3058	9.16	<1	326	820
BC	4/19/2000[2]	ND	ND	ND	ND	ND	0.08	ND	ND	ND	ND	ND	ND	5	15.3	8.0	1601	9.03	<1	224	414
BC	5/24/2000	ND	ND	ND	ND	ND	0.12	ND	0.09	ND	ND	0.09	ND	5	18.0	8.2	3103	6.8	<1	360	750
BC	6/13/2000	ND	ND	ND	ND	ND	0.10	ND	ND	ND	0.07	ND	ND	0	19.9	8.1	3034	6.85	<1	292	388
BC	7/12/2000	ND	ND	ND	ND	ND	0.33	ND	ND	ND	ND	ND	ND		18.5	8.3	3150	6.46			
BC	8/1/2000	ND	ND	ND	ND	ND	0.15	ND	ND	ND	ND	ND	ND		22.1	8.3	3300	6.71			
BC	9/6/2000	ND	ND	ND	ND	ND	0.10	ND		ND	0.17				19.2	8.1	3019	7.45			
BC	10/18/2000	ND	ND	ND	ND	ND	0.22	ND		ND	ND				17.7	8.0	3195	7.08			
BC	11/15/2000	ND	ND	ND	ND	ND	0.05	ND		0.06	ND				8.5	8.2	3237	10.64			
BC	12/5/2000	ND	ND	ND	ND	ND	0.19	ND		ND	ND				12.1	7.9	3302	8.45			
BC	1/17/2001	ND	ND	ND	ND	ND	0.25	ND		ND	ND				10.4	7.3	2271	8.08			
BC	4/25/2001	ND	ND	ND	ND	ND	0.08	ND		ND	ND				15.5	7.8	2935	6.39			
BC	5/16/2001	ND	ND	ND	ND	ND	0.05	ND		ND	ND				17.1	8.1	3120	6.5			
BC	6/12/2001	ND	ND	ND	ND	ND	0.08	ND		ND	ND				18.6	7.7	3457	5.56			
BC	7/24/2001	ND	ND	ND	ND	ND	0.20	ND		ND	ND				19.5	7.9	3311	5.97			
BC	8/22/2001	ND	ND	ND	ND	ND	0.11	ND		ND	ND				19.5	8.0	1732	7.03			
BC	9/25/2001	ND	ND	ND	ND	ND	0.05	ND		ND	ND				19.9	7.1	3389	8.15			
BC	10/16/2001	ND	ND	ND	ND	ND	0.07	ND		ND	ND				17.6	7.6	3487	7.58			
BC	11/28/2001	ND	ND	ND	ND	ND	0.09	ND		ND	ND				9.6	7.7	2950	9.05			
BC	12/18/2001	ND	ND	ND	ND	ND	0.08	ND		ND	ND				7.8	7.7	2938	10.37			
BC	1/8/2002	ND	ND	ND	ND	ND	0.08	ND		ND	ND				10.4	8.0	3195	8.71			
BC	2/14/2002	ND	ND	ND	ND	ND	0.13	ND		ND	ND				9.7	7.8	3374	9.32			
BC	3/12/2002	ND	ND	ND	ND	ND	0.08	ND		ND	ND				13.5	7.6	3069	8.74			

BC	4/18/2002	ND	ND	ND	ND	ND	0.09	ND	ND	ND	13.8	6.6	3053	6.75
BC	5/29/2002	ND	ND	ND	ND	ND	0.38	ND	ND	ND	16.9	7.8	3244	15.79
BC	6/12/2002	ND	ND	ND	ND	ND	ND	ND	ND	ND	19.0	8.0	3267	7.19
BC	8/14/2002	ND	ND	ND	ND	ND	0.08	ND	ND	ND	21.9	7.4	3270	5.95

* =survival significantly less than the control group (P< 0.05)
** =survival not significantly different from control due to replicate variability
† =greater than the LC50 for C. dubia

[1] = 0.30 inches of precipitation fell on 2/23/2000
[2] = 0.40 inches of precipitation fell on 4/18/2000

Site E San Diego Creek

Site	Date	Bifenthrin	Fenoxycarb	Hydramethylnon	Pyriproxyfen	Chlorpyrifos	Diazinon	Dimethoate	Fonophos	Malathion	Methidathion	Methyl Parathion	Phosmet	Percent Mortality	Temp. °C	pH	EC (µS/cm)	DO (mg/L)	Ammonia mg/L NH3	Alkalinity mg/L CaCO3	Hardness mg/L CaCO3
SDC	5/21/1999	ND	ND	ND	ND	ND	0.16	ND	ND	ND	ND	ND	ND	0	20.0	7.9	2960	10.4	NT	258	763
SDC	6/25/1999	ND	ND	ND	ND	ND	0.13	ND	ND	ND	ND	ND	ND	0	25.0	7.6	2740	8.4	NT	216	684
SDC	9/23/1999	ND	ND	ND	ND	ND	0.13	ND	ND	ND	ND	ND	ND	30	23.0	NT	2600	10.65	<1	234	700
SDC	10/27/1999	ND	ND	ND	ND	0.58†	0.16	0.45	ND	ND	ND	ND	ND	100*	20.6	8.5	2910	9.55	NT	236	732
SDC	12/9/1999	ND	ND	ND	ND	0.12	0.19	0.09	ND	ND	ND	ND	ND	100*	12.1	8.6	3105	13.9	<1	330	890
SDC	1/18/2000	ND	ND	ND	ND	0.08	0.13	ND	ND	ND	ND	ND	ND	100*	16.1	8.2	2985	13.11	<1	310	770
SDC	2/24/2000[1]	ND	ND	ND	ND	0.10	0.14	0.14	ND	0.07	ND	ND	ND	100*	11.1	7.8	879	9.83	<1	96	230
SDC	3/28/2000	ND	ND	ND	ND	ND	0.17	ND	ND	ND	ND	ND	ND	95*	19.1	8.5	2389	10.68	<1	168	574
SDC	4/19/2000[2]	ND	ND	ND	ND	0.06	0.20	0.20	0.07	0.07	ND	ND	ND	100*	17.8	7.7	16.27	7.89	<1	146	418
SDC	5/24/2000	ND	ND	ND	ND	ND	0.08	ND	0.06	ND	ND	ND	ND	20	22.1	8.5	2866	8.7	<1	224	756
SDC	6/13/2000	ND	ND	ND	ND	ND	0.07	ND	ND	ND	ND	ND	ND	20	26.3	8.7	3081	13.38	<1	178	138
SDC	7/13/2000	ND	ND	ND	ND	ND	0.09	ND	ND	ND	ND	ND	ND	30*	24.0	8.6	3253	11.66	3.68	180	742
SDC	8/2/2000	ND	ND	ND	ND	ND	0.16	0.12	ND	ND	ND	ND	ND	10	27.6	8.6	2878	16.3	0.06	180	650
SDC	9/7/2000[3]	ND	ND	ND	ND	ND	0.10	ND		ND	ND			10	21.2	8.1	3085	7.68	0.11	236	84
SDC	10/18/2000	ND	ND	ND	ND	ND	0.09	ND		ND	ND			0	21.2	8.3	2872	8.47	<1	254	750
SDC	11/16/2000	ND	ND	ND	ND	0.28†	0.09	ND		ND	ND			100*	13.9	8.4	2924	11.23	<0.1	246	754
SDC	12/6/2000	ND	ND	ND	ND	0.05	0.10	ND		ND	ND			100*	14.8	7.9	2992	10.47	0.17	280	772
SDC	1/18/2001	ND	ND	ND	ND	ND	0.08	ND		ND	ND			55*	10.7	7.2	3170	9.2	0.17	294	898
SDC	2/28/2001[4]	0.07	ND	ND	ND	ND	0.19	ND		ND	ND			100*	11.8	7.6	882	10.22	NA	108	256
SDC	3/20/2001	ND	ND	ND	ND	ND	0.06	ND		ND	ND			5	19.6	7.8	3168	11.13	NA	214	788
SDC	4/25/2001	ND	ND	ND	ND	ND	0.10	ND		ND	ND			0	22.8	7.4	3097	10.35	NA	198	716
SDC	5/16/2001	ND	ND	ND	ND	ND	ND	ND		ND	ND			5	21.4	8.3	3341	7.04	NA	234	376
SDC	6/13/2001	ND	ND	ND	ND	ND	0.06	ND		ND	ND			0	23.0	7.9	3021	10.17	<1	242	708
SDC	7/25/2001	ND	ND	ND	ND	ND	0.11	ND		ND	ND			10	24.6	8.4	3024	9.62	<1	226	624
SDC	8/22/2001	ND	ND	ND	ND	ND	0.10	ND		ND	ND			0	25.8	7.4	3132	8.02	NA	84	146
SDC	9/25/2001	ND	ND	ND	ND	ND	0.05	ND		ND	ND				24.7	7.1	3234	9.47			
SDC	10/16/2001	ND	ND	ND	ND	ND	0.07	ND		ND	ND				21.5	7.6	2939	7.71			
SDC	11/28/2001	ND	ND	ND	ND	0.14†	0.31	ND		ND	ND				12.1	7.7	2421	8.81			

SDC	12/18/2001	ND	ND	ND	ND	ND	0.29	ND	ND	ND	10.5	8.0	2488	11.84
SDC	1/8/2002	ND	ND	ND	ND	ND	0.08	ND	ND	ND	3.9	8.1	2166	10.2
SDC	2/14/2002	ND	ND	ND	ND	ND	0.08	ND	ND	ND	14.0	8.0	2894	10.84
SDC	3/12/2002	ND	ND	ND	ND	ND	ND	ND	ND	ND	19.4	7.5	3006	8.82
SDC	4/18/2002	ND	ND	ND	ND	ND	0.10	ND	ND	ND	18.6	8.2	2647	8.86
SDC	5/29/2002	ND	ND	ND	ND	ND	0.06	ND	ND	ND	23.8	8.1	2655	12.59
SDC	6/12/2002	ND	ND	ND	ND	ND	ND	ND	ND	ND	25.6	8.0	2839	11.12
SDC	8/14/2002	ND	ND	ND	ND	ND	0.06	ND	ND	ND	28.9	7.7	2900	12.6

* =survival significantly less than the control group (P< 0.05)
** =survival not significantly different from control due to replicate variability
† =greater than the LC50 for C. dubia

[1] = 0.30 inches of precipitation fell on 2/23/2000
[2] = 0.40 inches of precipitation fell on 4/18/2000
[3]= 0.02 inches of precipitation
[4]= 0.26 inches of precipitation; 0.38 inches of precipitation fell on 2/27/2001

Site F Hines Channel/ Central Irvine Channel

Site	Date	Bifenthrin	Fenoxycarb	Hydramethylnon	Pyriproxyfen	Chlorpyrifos	Diazinon	Dimethoate	Fonophos	Malathion	Methidathion	Methyl Parathion	Phosmet	Percent Mortality	Temp. °C	pH	EC (µS/cm)	DO (mg/L)	Ammonia mg/L NH3	Alkalinity mg/L CaCO3	Hardness mg/L CaCO3
Hines	5/21/1999	1.67†	ND	ND	ND	0.25†	1.94†	3.88	ND	0.32	ND	ND	ND	100*	17.0	7.4	2280	9.6	NT	110	740
Hines	6/25/1999	0.25†	ND	ND	ND	0.10	0.79†	ND	ND	2.57†	ND	0.09	ND	100*	31.0	7.9	408	7.7	NT	112	624
Hines	9/23/1999	0.24†	ND	ND	ND	0.32†	0.19	2.82	ND	ND	ND	ND	ND	100*	23.5	NT	2250	6.79	<1	162	860
Hines	10/27/1999	ND	ND	ND	ND	ND	0.12	0.09	ND	0.14	ND	ND	ND	100*	22.6	7.6	1460	7.5	NT	138	532
Hines	12/9/1999	0.63†	ND	ND	ND	0.12	0.57†	0.60	ND	0.09	ND	ND	ND	100*	14.5	8.3	1581	9.05	<1	240	480
Hines	1/18/2000	0.55†	ND	ND	ND	0.08	0.14	ND	ND	ND	ND	ND	ND	0	16.2	8.1	2000	7.51	<1	188	604
Hines	2/24/2000[1]	1.08†	ND	ND	ND	ND	0.79†	ND	ND	ND	ND	ND	ND	100*	12.6	7.4	1036	9.82	3.53	80	350
Hines	3/28/2000	2.03†	0.49	ND	ND	ND	0.06	ND	ND	ND	ND	ND	ND	100*	14.2	8.5	2595	7.35	<1	70	846
Hines	4/19/2000[2]	0.67†	ND	ND	ND	ND	0.32	ND	ND	ND	ND	ND	ND	100*	25.7	7.5	1577	5.03	3.34	58	524
Hines	5/24/2000[3]	0.50†	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10	21.4	8.7	1914	7.09	<1	232	900
Hines	6/13/2000	0.39†	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	100*	32.5	8.1	3160	6.65	>10	258	140
Hines	7/12/2000	0.27†	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		21.4	8.2	3298	8.45			
Hines	9/7/2000	0.57†	ND	ND	ND	ND	ND	ND		ND	ND				27.1	8.4	3510	6.27			
Hines	10/18/2000	0.07	ND	ND	ND	ND	ND	ND		ND	ND				21.4	8.7	2237	6.21			
Hines	11/15/2000	0.12†	ND	ND	ND	0.06	0.05	ND		ND	ND				16.1	8.7	2217	9.85			
Hines	12/5/2000	0.14†	ND	ND	ND	ND	ND	ND		ND	ND				16.0	8.6	1800	12			
Hines	1/17/2001	0.34†	ND	ND	ND	ND	ND	ND		ND	ND				5.6	8.1	1425	11.08			
Hines	2/28/2001[4]	0.93†	ND	ND	ND	ND	ND	ND		0.14	ND				11.4	7.3	660	10.57			
Hines	3/20/2001	0.49†	ND	ND	ND	ND	0.06	ND		0.07	ND				28.4	7.6	2878	5.48			
Hines	4/25/2001	0.85†	ND	ND	ND	ND	ND	ND		ND	ND				23.8	7.4	3233	5.7			
Hines	5/15/2001	0.37†	ND	ND	ND	ND	ND	ND		0.16	ND				27.5	7.9	2307	5.66			
Hines	6/12/2001	0.26†	ND	ND	ND	ND	ND	ND		0.10	ND				24.3	7.9	2401	7.1			
Hines	7/24/2001	0.40†	ND	ND	ND	ND	ND	ND		ND	ND				32.8	6.8	2007	7.33			
Hines	8/22/2001	0.39†	ND	ND	ND	ND	ND	ND		ND	ND				29.1	7.8	1551	8.59			
Hines	9/25/2001	0.11†	ND	ND	ND	ND	ND	ND		ND	ND				31.8	7.9	3066	7.51			
Hines	10/16/2001	0.20†	ND	ND	ND	ND	ND	ND		ND	ND				17.9	8.3	1997	7.98			
Hines	11/28/2001	0.53†	ND	ND	ND	ND	ND	ND		0.11	ND				11.6	8.2	2020	9.95			

Hines	12/18/2001	0.17†	ND	ND	ND	ND	ND	ND	ND	ND	7.6	8.2	815	11.26
Hines	1/8/2002	0.16†	ND	ND	ND	ND	ND	ND	ND	ND	11.1	8.1	1280	10.54
Hines	2/14/2002	0.64†	ND	ND	ND	ND	ND	ND	ND	ND	13.0	8.0	2356	9.48
Hines	3/12/2002	0.36†	ND	ND	ND	ND	ND	ND	ND	ND	15.0	8.2	2400	8.95
Hines	4/18/2002	0.42†	ND	ND	ND	ND	ND	ND	ND	ND	16.4	7.9	2485	8.2
Hines	5/29/2002	0.28†	ND	ND	ND	ND	ND	ND	0.09	ND	22.3	7.7	1441	7.97
Hines	6/12/2002	0.13†	ND	ND	1.32	ND	ND	ND	ND	ND	28.5	8.1	1460	6.4
Hines	8/14/2002	0.19†	ND	ND	ND	ND	ND	ND	ND	ND	35.4	8.2	3300	6.68

* =survival significantly less than the control group (P< 0.05)
** =survival not significantly different from control due to replicate variability
† =greater than the LC50 for C. dubia

[1] = 0.63 inches of rain fell on 2/23/2000
[2] = 0.18 inches of rain fell on 4/18/2000
[3] = 0.05 inches of rain fell on 5/24/2000
[4] = 0.32 inches of rain fell on 2/28/2001; 0.42 inches of rain fell on 2/27/2001

Site G El Modeno Gardens

Site	Date	Bifenthrin	Fenoxycarb	Hydramethylnon	Pyriproxyfen	Chlorpyrifos	Diazinon	Dimethoate	Fonophos	Malathion	Methidathion	Methyl Parathion	Phosmet	Percent Mortality	Temp. °C	pH	EC (µS/cm)	DO (mg/L)	Ammonia mg/L NH3	Alkalinity mg/L CaCO3	Hardness mg/L CaCO3
EM	6/25/1999	ND	0.71	ND	ND	ND	1.31†	ND	ND	0.59	ND	0.12	ND	100*	NT	7.8	1790	NT	NT	94	664
EM	9/23/1999	1.12†	ND	ND	ND	ND	0.64†	ND	ND	1.24†	ND	ND	ND	100*	26.4	NT	1675	9.05	<1	148	520
EM	10/27/1999	0.48†	ND	ND	ND	ND	2.01†	ND	ND	1.74†	ND	ND	ND	100*	26.8	8.7	1540	10.98	NT	116	516
EM	12/9/1999	3.12†	ND	ND	ND	ND	0.34	ND	0.06	0.06	ND	ND	ND	100*	15.8	7.6	1902	8.89	4.25	200	650
EM	1/18/2000	0.69†	ND	ND	ND	ND	0.09	ND	0.09	ND	ND	ND	ND	0	14.1	8.6	1771	10.5	<1	190	582
EM	2/24/2000[1]	1.94†	ND	ND	ND	ND	7.99†	ND	ND	ND	ND	0.17	ND	100*	9.5	8.1	1467	9.47	13	124	510
EM	3/28/2000	0.43†	ND	ND	ND	ND	0.13	ND	ND	ND	ND	ND	ND	100*	14.5	8.5	2417	11.07	<1	130	718
EM	4/19/2000[2]	0.47†	ND	ND	ND	ND	2.32†	ND	ND	ND	ND	ND	ND	100*	28.1	8.8	1838	8.4	<1	116	600
EM	5/24/2000[3]	0.98†	ND	ND	ND	0.06	0.31	ND	ND	0.19	ND	ND	ND	100*	20.7	8.4	1570	7.18	<1	150	500
EM	6/13/2000	0.45†	ND	ND	ND	ND	0.09	ND	ND	ND	0.09	ND	ND	100*	31.2	7.8	2566	6.11	>10	186	142
EM	7/12/2000	0.27†	ND	ND	ND	ND	0.10	ND	ND	ND	ND	ND	ND		26.0	8.6	1489	8.22			
EM	8/2/2000	0.24†	ND	ND	ND	ND	0.07	ND	ND	0.06	ND	ND	ND		24.9	8.2	2312	7.21			
EM	9/7/2000	0.22†	ND	ND	ND	ND	0.09	ND		0.10	ND			30	17.1	8.1	2025	6.36	1.36	158	128
EM	10/18/2000	0.31†	ND	ND	ND	0.09	ND	0.09		ND	ND				17.7	8.4	1858	8.51			
EM	11/16/2000	0.31†	ND	ND	ND	0.05	ND	ND		ND	ND				10.6	8.5	1273	13.71			
EM	12/5/2000	0.57†	ND	ND	ND	0.07	ND	ND		ND	ND				17.3	7.9	2250	9.51			
EM	1/18/2001	1.24†	ND	ND	ND	ND	0.05	ND		ND	ND				9.3	8.0	1527	11.06			
EM	2/28/2001[4]	2.41†	ND	ND	ND	ND	0.06	ND		0.20	ND				10.9	7.9	860	10.4			
EM	3/20/2001	0.83†	ND	ND	ND	0.07	ND	ND		ND	ND				22.6	7.6	2618	9.69			
EM	5/15/2001	0.37†	ND	ND	ND	ND	ND	ND		0.08	ND				27.3	7.8	1989	9.98			
EM	6/12/2001	0.23†	ND	ND	ND	ND	0.04	ND		0.57	ND				22.7	7.1	2972	8.2			
EM	8/1/2001	0.49†	ND	ND	ND	0.04	ND	ND		ND	ND				21.1	7.2	2648	4.65			
EM	8/22/2001	0.69†	ND	ND	ND	ND	ND	ND		ND	ND				26.9	7.1	2854	5.75			
EM	9/25/2001	0.50†	ND	ND	ND	ND	ND	ND		0.13	ND				25.6	6.6	2540	2.93			
EM	10/16/2001	0.32†	ND	ND	ND	ND	ND	ND		17.44†	ND				19.4	6.6	2219	5.47			
EM	11/28/2001	0.24†	ND	ND	ND	ND	ND	ND		0.17	ND				12.8	7.0	1875	8.14			
EM‡	12/18/2001	0.46†	ND	ND	ND	ND	ND	ND		ND	ND				12.8	7.5	1855	9.78			

EM‡	1/8/2002	0.56†	ND	ND	ND	ND	ND	ND	ND	ND	11.8	7.8	1795	9.84
EM	2/14/2002	0.53†	ND	ND	ND	ND	ND	ND	ND	ND	17.5	6.5	2580	6.23
EM	4/18/2002	1.19†	ND	ND	ND	ND	0.05	ND	0.66	ND	22.5	6.6	2042	9.51
EM	5/29/2002	0.50†	ND	ND	ND	ND	ND	ND	0.06	ND	24.6	7.0	1537	8.97
EM	6/12/2002	0.49†	ND	ND	ND	ND	ND	ND	0.09	ND	27.0	7.0	4096	4.94
EM	8/14/2002	1.69†	ND	ND	ND	ND	ND	ND	ND	ND	29.3	7.2	2900	6.86

* =survival significantly less than the control group (P< 0.05)
** =survival not significantly different from control due to replicate variability
† =greater than the LC50 for C. dubia
‡ =sample was taken at storm water overflow prior to vegetative filter strip

[1] = 0.63 inches of rain fell on 2/23/2000
[2] = 0.18 inches of rain fell on 4/18/2000
[3] = 0.05 inches of rain fell on 5/24/2000
[4] = 0.32 inches of rain fell on 2/28/2001; 0.42 inches of rain fell on 2/27/2001

Site H Marshburn Slough

Site	Date	Bifenthrin	Fenoxycarb	Hydramethylnon	Pyriproxyfen	Chlorpyrifos	Diazinon	Dimethoate	Fonophos	Malathion	Methidathion	Methyl Parathion	Phosmet	Percent Mortality	Temp. °C	pH	EC (µS/cm)	DO (mg/L)	Ammonia mg/L NH3	Alkalinity mg/L CaCO3	Hardness mg/L CaCO3
MBS	2/24/2000[1]	0.37†	ND	ND	ND	0.06	0.29	ND	ND	2.44†	ND	ND	ND	100*	12.9	7.5	1599	10.58	5.96	40	550
MBS	10/18/2000	0.05	ND	ND	ND	ND	ND	ND		ND	ND				20.1	8.3	1313	NT			
MBS	11/15/2000	ND	ND	ND	ND	0.08	ND	ND		ND	ND				15.5	8.3	690	9.56			
MBS	12/5/2000	ND	0.41	ND	ND	ND	0.19	ND		1.01	ND				14.6	7.9	1352	9.04			
MBS	2/28/2001[2]	1.95†	ND	ND	ND	ND	0.07	ND		0.78	ND				12.0	6.7	926	10.62			

* =survival significantly less than the control group (P< 0.05)
** =survival not significantly different from control due to replicate variability
† =greater than the LC50 for C. dubia

[1] = 0.63 inches of rain fell on 2/23/2000
[2] = 0.32 inches of rain fell on 2/28/2001; 0.42 inches of rain fell on 2/27/2001

Site I San Juan Creek

Site	Date	Bifenthrin	Fenoxycarb	Hydramethylnon	Pyriproxyfen	Chlorpyrifos	Diazinon	Dimethoate	Fonophos	Malathion	Methidathion	Methyl Parathion	Phosmet	Percent Mortality	Temp. °C	pH	EC (µS/cm)	DO (mg/L)	Ammonia mg/L NH3	Alkalinity mg/L CaCO3	Hardness mg/L CaCO3
SJC	5/21/1999	ND	ND	ND	ND	ND	0.06	ND	ND	ND	ND	ND	ND	0	21.0	7.8	2580	17.2	NT	191	880
SJC	9/23/1999	ND	ND	ND	ND	ND	0.06	ND	ND	ND	ND	ND	ND	100*	20.3	NT	2940	8.13	<1	386	805
SJC	10/26/1999	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5	27.1	7.9	3030	NT	<0.50	182	647
SJC	12/9/1999	ND	ND	ND	ND	ND	0.05	ND	ND	ND	ND	ND	ND	60*	12.4	7.7	1254	15.07	<1	1440	1150
SJC	1/17/2000	ND	ND	ND	ND	ND	ND	ND	0.05	ND	ND	ND	ND	100*	17.0	8.7	2735	16.66	<1	162	324
SJC	2/23/2000[1]	ND	ND	ND	ND	0.05	0.13	ND	ND	0.07	ND	ND	ND	10	13.1	8.2	980	10.45	<1	80	276
SJC	3/27/2000	ND	ND	ND	ND	ND	0.05	ND	ND	ND	ND	ND	ND	5	19.4	8.4	2126	14.84	<1	92	780
SJC	4/19/2000[2]	ND	ND	ND	ND	ND	0.19	0.13	ND	ND	ND	ND	ND	0	17.2	8.2	1294	8.5	<1	60	58
SJC	5/24/2000	ND	ND	ND	ND	ND	ND	ND	0.05	ND	ND	ND	ND	100*	19.3	8.2	2657	8.87	<1	96	780
SJC	6/13/2000	ND	ND	ND	ND	ND	ND	ND	0.04	ND	ND	ND	ND	0	25.1	8.0	2662	10.5	<1	208	140
SJC	8/1/2000	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		25.3	8.4	2974	11.75			
SJC	9/6/2000	ND	ND	ND	ND	ND	ND	ND		ND	ND				22.0	8.2	2660	13.26			
SJC	10/18/2000	ND	ND	ND	ND	ND	ND	ND		ND	ND				20.0	8.1	2563	13.27			
SJC	11/15/2000	ND	ND	ND	ND	ND	0.07	ND		ND	ND				19.2	8.5	2367	12.37			
SJC	12/5/2000	ND	ND	ND	ND	ND	0.08	ND		ND	ND				19.3	8.1	2557	11.77			
SJC	1/17/2001	ND	ND	ND	ND	ND	0.07	ND		ND	ND				13.8	7.4	2190	9			

* =survival significantly less than the control group (P< 0.05)

** =survival not significantly different from control due to replicate variability

† =greater than the LC50 for C. dubia

[1] = 0.02 inches of rain fell on 2/23/2000; 0.95 inches of rain fell on 2/22/2000

[2] = 0.73 inches of rain fell on 4/18/2000

Site J Arroyo Trabuco at Oso Parkway

Site	Date	Bifenthrin	Fenoxycarb	Hydramethylnon	Pyriproxyfen	Chlorpyrifos	Diazinon	Dimethoate	Fonophos	Malathion	Methidathion	Methyl Parathion	Phosmet	Percent Mortality	Temp. °C	pH	EC (µS/cm)	DO (mg/L)	Ammonia mg/L NH3	Alkalinity mg/L CaCO3	Hardness mg/L CaCO3
Oso	5/21/1999	ND	0.51	0.29	1.34	ND	ND	ND	ND	ND	ND	ND	ND	10	19.0	7.9	900	10.2	NT	174	326
Oso	6/25/1999	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	26.0	8.0	879	8.4	NT	156	324
Oso	9/23/1999	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	20.2	NT	9.14	8.17	<1	200	330
Oso	10/26/1999	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	15	20.7	7.8	906	8.2	<0.50	168	310
Oso	12/9/1999	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	13.8	7.6	455	10.04	<1	250	350
Oso	1/17/2000	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	100*	16.5	8.3	940	11.82	<1	242	770
Oso	2/23/2000[1]	0.09†	ND	ND	ND	0.17†	0.19	ND	ND	ND	ND	ND	ND	100*	12.3	8.0	226	10.27	<1	44	82
Oso	3/27/2000	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10	17.3	8.6	902	10.6	<1	148	314
Oso	4/19/2000[2]	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	17.4	7.8	760	8.28	<1	162	306
Oso	5/24/2000	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20	18.3	8.0	957	8.12	<1	176	336
Oso	6/13/2000	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	20.3	8.0	955	8.92	<1	180	136
Oso	8/1/2000	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND		22.7	8.1	945	9.22			
Oso	9/6/2000	ND	ND	ND	ND	ND	ND	ND		ND	ND				20.1	8.2	817	10.06			
Oso	10/18/2000	ND	ND	ND	ND	ND	ND	ND		ND	ND				18.6	8.1	960	9.12			
Oso	11/15/2000	ND	ND	ND	ND	ND	ND	ND		ND	ND				16.0	7.8	964	9.07			
Oso	12/5/2000	ND	ND	ND	ND	ND	ND	ND		ND	ND				16.1	7.7	960	8.67			
Oso	1/17/2001	ND	ND	ND	ND	ND	ND	ND		ND	ND				14.6	7.2	947	8.5			

* =survival significantly less than the control group (P< 0.05)
** =survival not significantly different from control due to replicate variability
† =greater than the LC50 for C. dubia

[1] = 0.02 inches of rain fell on 2/23/2000; 0.95 inches of rain fell on 2/22/2000
[2] = 0.73 inches of rain fell on 4/18/2000

January 2000 Rain Event Results

Site	Time	Bifenthrin	Fenoxycarb	Hydramethylnon	Pyriproxyfen	Chlorpyrifos	Diazinon	Dimethoate	Fonophos	Malathion	Methidathion	Methyl Parathion	Phosmet	Percent Mortality	Temp. °C	pH	EC (µS/cm)	Ammonia ppb NH3	Alkalinity mg/L CaCO3	Hardness mg/L CaCO3	Discharge (CFS)
BC	1510	ND	ND	ND	ND	ND	0.46	ND	ND	0.21	ND	ND	ND	100*	15.4	8.0	2379	<1	188	500	
	1630	ND	ND	ND	ND	ND	0.63†	ND	ND	0.29	ND	ND	ND	100*	NT	7.9	2252	<1	178	580	
	1750	ND	ND	ND	ND	ND	0.52†	ND	ND	0.31	ND	ND	ND	100*	NT	7.9	1990	<1	174	410	
	1920	ND	ND	ND	ND	ND	0.52†	ND	ND	0.25	ND	ND	ND	100*	15.2	7.8	1944	<1	176	410	
	2240	ND	ND	ND	ND	ND	0.38	ND	ND	0.25	ND	ND	ND	100*	NT	7.8	1965	<1	188	430	
	5	ND	ND	ND	ND	ND	0.40	ND	ND	0.22	ND	ND	ND	100*	14.9	7.8	1975	<1	186	390	
EM	1515	2.57†	ND	ND	ND	ND	0.84†	ND	ND	0.18	ND	ND	ND	100*	17.2	8.2	1866	1.82	112	660	0.12
	1642	2.67†	ND	ND	ND	ND	0.40	ND	ND	0.09	ND	ND	ND	100*	16.4	8.2	2075	1.24	120	750	0.07
	1833	0.79†	ND	ND	ND	0.06	0.13	ND	ND	ND	ND	ND	ND	100*	15.6	7.9	1082	1.94	80	310	0.45
	1934	1.4†	ND	ND	ND	ND	0.92†	ND	ND	0.32	ND	ND	ND	100*	15.5	8.1	1280	<1	88	460	0.61
	2333	1.8†	0.18	ND	ND	ND	0.60†	ND	ND	0.31	ND	ND	ND	100*	14.8	8.0	1478	1.43	82	540	1.19
	33	1.24†	ND	ND	ND	ND	0.53†	ND	ND	0.11	ND	ND	ND	100*	14.7	8.0	1966	1.92	40	220	0.79
HINES	1431	3.79†	ND	ND	ND	0.12	0.32	ND	ND	0.11	ND	ND	ND	100*	16.6	8.4	1424	1.21	74	490	0.52
	1600	2.06†	ND	ND	ND	ND	0.37	ND	ND	0.08	ND	ND	ND	100*	16.7	8.1	1527	<1	82	500	0.47
	1725	1.35†	ND	ND	ND	ND	0.32	ND	ND	0.07	ND	ND	ND	100*	15.9	8.0	1701	<1	84	580	0.26
	1900	0.319†	ND	ND	ND	ND	0.24	ND	ND	0.09	ND	ND	ND	100*	15.6	8.0	1634	1.02	90	460	0.85
	2255	2.45†	ND	ND	ND	0.08	0.20	ND	ND	0.09	ND	ND	ND	100*	15.1	7.8	1672	<1	88	540	44.39
	2355	1.93†	ND	ND	ND	0.35†	0.27	ND	ND	0.16	ND	ND	ND	100*	14.9	7.9	1452	1.06	68	460	10.35
MBS	1454	1.77†	0.22	ND	ND	0.12	0.15	ND	ND	0.10	ND	ND	ND	100*	16.5	7.4	3050	10.2	76	1170	2.96
	1620	2.27†	ND	ND	ND	0.06	0.18	ND	ND	0.14	ND	ND	ND	100*	16.7	7.6	3199	2.07	56	1160	1.49
	1815	5.3†	0.31	ND	ND	0.05	0.11	ND	ND	0.13	ND	ND	ND	100*	15.8	7.7	3190	6.25	60	1100	2.80
	1915	1.95†	ND	ND	ND	0.06	0.09	ND	ND	0.22	ND	ND	ND	100*	15.5	7.8	2807	2.15	64	930	3.05
	2315	2.06†	0.40	ND	ND	0.08	0.14	ND	ND	0.13	ND	ND	ND	100*	14.8	7.6	2120	1.4	46	720	10.62
	13	1.57†	0.34	ND	ND	0.09	0.20	ND	ND	0.18	ND	ND	ND	100*	14.7	7.7	2434	1.32	112	560	5.66

SDC	1450	ND	ND	ND	ND	0.12	0.59†	ND	ND	0.35	ND	ND	ND	100*	NT	8.0	688	2.44	64	176	210
	1615	ND	ND	ND	ND	ND	0.84†	0.06	ND	0.19	ND	ND	ND	100*	NT	7.9	804	1.82	70	250	185
	1732	ND	ND	ND	ND	0.11	0.57†	ND	ND	0.40	ND	ND	ND	100*	16.5	8.0	1046	<1	90	240	143
	1900	ND	ND	ND	ND	0.08	0.54†	ND	ND	0.53	ND	ND	ND	100*	16.4	8.0	988	1.29	88	210	128
	2215	ND	ND	ND	ND	0.16†	0.50	ND	ND	1.47†	ND	ND	ND	100*	16.4	7.9	870	1.01	84	180	79
	2350	ND	ND	ND	ND	0.21†	0.54†	ND	ND	0.25	ND	ND	ND	100*	16.2	7.8	870	<1	82	200	284
WCP	1420	ND	ND	ND	ND	0.11	0.68†	ND	ND	0.24	ND	ND	ND	100*	17.4	7.8	1250	2.94	32	64	
	1540	ND	ND	ND	ND	ND	1.08†	ND	ND	0.19	ND	ND	ND	100*	16.6	8.0	286.1	1.9	40	72	
	1700	ND	ND	ND	ND	0.06	1.08†	ND	ND	0.39	ND	ND	ND	100*	16	8.0	297.7	<1	40	100	
	1830	ND	ND	ND	ND	0.09	0.56†	ND	ND	0.20	ND	ND	ND	100*	16.2	7.7	510	1.94	64	82	
	2310	ND	ND	ND	ND	0.23†	0.69†	ND	ND	0.38	ND	ND	ND	100*	NT	7.4	175.8	1.16	30	50	
	30	ND	ND	ND	ND	0.10	0.60†	ND	ND	0.32	ND	ND	ND	100*	15.8	7.5	190.4	<1	32	40	
SJC	1630	ND	ND	ND	ND	ND	0.58†	ND	ND	0.43	ND	ND	ND	100*	NT	7.8	1194	1.14	108	270	
OSO	1650	ND	ND	ND	ND	0.08	0.59†	0.08	ND	0.11	ND	ND	ND	100*	NT	7.9	678	<1	100	220	

* =survival significantly less than the control group (P< 0.05)

† = greater than the LC50 for C. dubia

October 2000 Rain Event Results

Site	Time	Bifenthrin	Fenoxycarb	Hydramethylnon	Pyriproxyfen	Chlorpyrifos	Diazinon	Dimethoate	Fonophos	Malathion	Methidathion	Methyl Parathion	Phosmet	Percent Mortality	Temp. °C	pH	EC (µS/cm)	DO (mg/L)	Discharge (CFS)
SJC	645	0.16†	ND	ND	ND	0.34†	0.65†	0.08		0.36	ND				14.8	7.7	260	NT	
	820	ND	ND	ND	ND	ND	0.33	0.09		0.18	ND				14.9	8	309	NT	
	1030	ND	ND	ND	ND	ND	0.58†	ND		0.23	ND				15.8	7.9	583	NT	
	1150	ND	ND	ND	ND	ND	0.55†	ND		0.27	ND				15.7	7.9	639	NT	
	1350	ND	ND	ND	ND	ND	0.53†	ND		0.19	ND				17.9	7.9	750	NT	
	1510	ND	ND	ND	ND	ND	0.60†	ND		0.16	ND				18.0	7.9	774	NT	
OSO	550	ND	ND	ND	ND	0.05	0.24	ND		ND	ND				16.1	7.9	787	7.8	86
	740	0.10†	ND	ND	ND	0.18†	0.36	ND		0.12	ND				15.8	8.1	400	8.88	371
	1000	ND	ND	ND	ND	0.19†	0.32	ND		0.07	ND				16.0	7.8	356	8.56	297
	1050	ND	ND	ND	ND	0.24†	0.50	ND		0.14	ND				15.7	7.5	411	8.76	174
	1300	ND	ND	ND	ND	0.20†	0.43	ND		0.08	ND				16.6	7.9	513	7.92	69
	1425	ND	ND	ND	ND	0.19†	0.43	ND		0.05	ND				17.7	7.6	664	8.6	40

† = greater than the LC50 for C. dubia

Appendix C

Toxic Unit Calculations

Site	date	TU Bifenthrin	TU Chlorpyrifos	TU Diazinon	TU Malathion	TU Methidathion	TU sum of OP's
BCC	5/21/1999	0.00	0.00	0.14	0.00	0.00	0.14
BCC	6/25/1999	0.00	0.00	0.21	0.00	0.00	0.21
BCC	9/23/1999	0.00	0.00	0.44	0.00	0.00	0.44
BCC	10/27/1999	0.00	0.00	0.46	0.00	0.00	0.46
BCC	12/9/1999	0.00	0.00	0.41	0.00	0.00	0.41
BCC	2/23/2000	0.00	0.00	0.57	0.08	0.00	0.65
BCC	3/27/2000	0.00	0.00	0.16	0.00	0.00	0.16
BCC	4/19/2000	0.00	0.00	0.74	0.00	0.00	0.74
BCC	5/24/2000	0.00	0.00	0.37	0.00	0.00	0.37
BCC	6/13/2000	0.00	0.00	0.15	0.00	0.00	0.15
EGG	6/25/1999	0.00	0.00	0.22	0.00	0.00	0.22
EGG	9/23/1999	0.00	0.00	0.21	0.00	0.00	0.21
EGG	10/27/1999	0.00	0.00	0.00	0.00	0.00	0.00
EGG	12/9/1999	0.00	0.00	0.23	0.00	0.00	0.23
EGG	2/23/2000	0.00	3.15	0.27	0.07	0.00	3.49
EGG	3/27/2000	0.00	0.00	0.27	0.37	0.00	0.64
EGG	4/19/2000	0.00	0.00	0.20	0.00	0.00	0.20
EGG	5/24/2000	0.00	0.00	0.23	0.00	0.00	0.23
EGG	6/13/2000	0.00	0.00	0.14	0.00	0.00	0.14
WCP	12/9/1999	0.00	0.99	4.41	0.00	0.02	5.43
WCP	2/24/2000	0.00	0.00	0.34	0.13	0.00	0.48
WCP	4/19/2000	0.00	0.00	0.19	0.00	0.00	0.19
WCP	5/24/2000	0.00	0.00	0.62	0.00	0.04	0.66
WCP	6/13/2000	0.00	0.00	0.28	0.00	0.00	0.28
BC	9/23/1999	0.00	0.00	0.47	0.05	0.00	0.53
BC	10/27/1999	0.00	0.00	0.26	0.00	0.00	0.26
BC	12/9/1999	0.00	0.00	0.51	0.00	0.00	0.51
BC	2/24/2000	0.00	0.00	0.14	0.00	0.00	0.14
BC	3/28/2000	0.00	0.00	0.10	0.00	0.00	0.10
BC	4/19/2000	0.00	0.00	0.15	0.00	0.00	0.15
BC	5/24/2000	0.00	0.00	0.24	0.00	0.00	0.24
BC	6/13/2000	0.00	0.00	0.19	0.00	0.03	0.22
SDC	5/21/1999	0.00	0.00	0.31	0.00	0.00	0.31
SDC	6/25/1999	0.00	0.00	0.26	0.00	0.00	0.26
SDC	9/23/1999	0.00	0.00	0.26	0.00	0.00	0.26
SDC	10/27/1999	0.00	4.46	0.31	0.00	0.00	4.78
SDC	12/9/1999	0.00	0.95	0.37	0.00	0.00	1.32
SDC	2/24/2000	0.00	0.78	0.26	0.06	0.00	1.10
SDC	3/28/2000	0.00	0.00	0.33	0.00	0.00	0.33
SDC	4/19/2000	0.00	0.48	0.39	0.06	0.00	0.93
SDC	5/24/2000	0.00	0.00	0.15	0.00	0.00	0.15
SDC	6/13/2000	0.00	0.00	0.15	0.00	0.00	0.15
SDC	7/13/2000	0.00	0.00	0.17	0.00	0.00	0.17

Site	date	TU Bifenthrin	TU Chlorpyrifos	TU Diazinon	TU Malathion	TU Methidathion	TU sum of OP's
SDC	8/2/2000	0.00	0.00	0.32	0.00	0.00	0.32
SDC	9/7/2000	0.00	0.00	0.20	0.00	0.00	0.20
SDC	10/18/2000	0.00	0.00	0.18	0.00	0.00	0.18
SDC	11/16/2000	0.00	2.15	0.18	0.00	0.00	2.34
SDC	12/6/2000	0.00	0.42	0.20	0.00	0.00	0.62
SDC	1/18/2001	0.00	0.00	0.15	0.00	0.00	0.15
SDC	2/28/2001	0.91	0.00	0.37	0.00	0.00	0.37
SDC	3/20/2001	0.00	0.00	0.12	0.00	0.00	0.12
SDC	4/25/2001	0.00	0.00	0.19	0.00	0.00	0.19
SDC	5/16/2001	0.00	0.00	0.00	0.00	0.00	0.00
SDC	6/13/2001	0.00	0.00	0.13	0.00	0.00	0.13
SDC	7/25/2001	0.00	0.00	0.21	0.00	0.00	0.21
SDC	8/22/2001	0.00	0.00	0.19	0.00	0.00	0.19
Hines	5/21/1999	21.41	1.92	3.80	0.28	0.00	6.01
Hines	6/25/1999	3.21	0.79	1.55	2.25	0.00	4.60
Hines	9/23/1999	3.08	2.46	0.37	0.00	0.00	2.84
Hines	10/27/1999	0.00	0.00	0.23	0.12	0.00	0.35
Hines	12/9/1999	8.08	0.90	1.12	0.08	0.00	2.10
Hines	2/24/2000	13.85	0.00	1.55	0.00	0.00	1.55
Hines	3/28/2000	26.03	0.00	0.12	0.00	0.00	0.12
Hines	4/19/2000	8.59	0.00	0.63	0.00	0.00	0.63
Hines	5/24/2000	6.41	0.00	0.00	0.00	0.00	0.00
Hines	6/13/2000	5.00	0.00	0.00	0.00	0.00	0.00
EM	6/25/1999	0.00	0.00	2.57	0.52	0.00	3.09
EM	9/23/1999	14.36	0.00	1.25	1.09	0.00	2.34
EM	10/27/1999	6.15	0.00	3.94	1.53	0.00	5.47
EM	12/9/1999	40.00	0.00	0.66	0.05	0.00	0.71
EM	2/24/2000	24.87	0.00	15.67	0.00	0.00	15.67
EM	3/28/2000	5.51	0.00	0.26	0.00	0.00	0.26
EM	4/19/2000	6.03	0.00	4.55	0.00	0.00	4.55
EM	5/24/2000	12.56	0.44	0.61	0.17	0.00	1.21
EM	6/13/2000	5.77	0.00	0.17	0.00	0.04	0.21
MBS	2/24/2000	4.74	0.43	0.57	2.14	0.00	3.14
SJC	5/21/1999	0.00	0.00	0.11	0.00	0.00	0.11
SJC	9/23/1999	0.00	0.00	0.12	0.00	0.00	0.12
SJC	10/26/1999	0.00	0.00	0.00	0.00	0.00	0.00
SJC	12/9/1999	0.00	0.00	0.10	0.00	0.00	0.10
SJC	2/23/2000	0.00	0.41	0.25	0.06	0.00	0.73
SJC	3/27/2000	0.00	0.00	0.09	0.00	0.00	0.09
SJC	4/19/2000	0.00	0.00	0.37	0.00	0.00	0.37
SJC	5/24/2000	0.00	0.00	0.00	0.00	0.00	0.00
SJC	6/13/2000	0.00	0.00	0.00	0.00	0.00	0.00
OSO	5/21/1999	0.00	0.00	0.00	0.00	0.00	0.00

Site	date	TU Bifenthrin	TU Chlorpyrifos	TU Diazinon	TU Malathion	TU Methidathion	TU sum of OP's
OSO	6/25/1999	0.00	0.00	0.00	0.00	0.00	0.00
OSO	9/23/1999	0.00	0.00	0.00	0.00	0.00	0.00
OSO	10/26/1999	0.00	0.00	0.00	0.00	0.00	0.00
OSO	12/9/1999	0.00	0.00	0.00	0.00	0.00	0.00
OSO	2/23/2000	1.15	1.31	0.36	0.00	0.00	1.67
OSO	3/27/2000	0.00	0.00	0.00	0.00	0.00	0.00
OSO	4/19/2000	0.00	0.00	0.00	0.00	0.00	0.00
OSO	5/24/2000	0.00	0.00	0.00	0.00	0.00	0.00
OSO	6/13/2000	0.00	0.00	0.00	0.00	0.00	0.00